Distribution of Bacillariophyceae in the Avon-Heathcote Estuary, Christchurch, New Zealand and their use as palaeoenvironmental indicators

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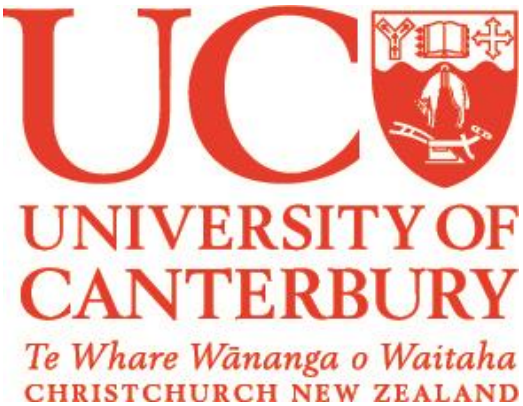

ABSTRACT

The Avon-Heathcote Estuary/Ihutai (AHE) is located on the east coast of New Zealand's South Island, just north of Banks Peninsula. Over the last ~150 years the AHE has undergone change caused by the rapid settlement of European immigrants, extensive land use changes and the industrialisation of society. Estuaries are one of the most important ecological areas and also one of the area's most built around areas by humans. For this reason it is important that the impacts which anthropogenic activities can have on the environment, and in particular primary producing biota are understood. This knowledge will assist with developing effective remediation processes for already damaged areas and assist in producing future communities that are environmentally friendly. While there is a moderate pool of knowledge on the current situation with pollutants in the AHE the existing knowledge of Bacillariophyceae (diatoms) is extremely limited, and prior to this study, no data existed on diatom communities pre-dating European arrival or during the industrial development of Christchurch.

Modern diatom communities and environmental factors were studied in a spatial sense. Sediments collected along multiple transects around the AHE allowed a modern database to be developed containing information on trace metal concentrations, organic carbon concentration, variations in sediment size, salinity, pH and elevation changes for sample sites, as well as the structure of the AHE diatom community. Statistical analyses indicate that the modern diatom communities are relatively homogenous across the Estuary, as are the selected environmental factors. Very few correlations could be made between what little variance was recorded in diatom communities and the above environmental factors. Canonical correspondence analysis was also undertaken to determine how much of the variance seen in diatom species could be attributed to the selected environmental factors (traces metals, organic carbon, grain size, elevation). The results indicated that the above environmental factors have very little influence and the greatest influence over diatom distribution in the modern AHE is proximity to source waters of the Avon and Heathcote rivers.

Following the modern study a 270cm sediment core was collected from near the Avon River mouth to determine temporal change in diatom communities in response to urban development about the AHE. Over the past 150 years of industrial activity two significant changes have occurred in the diatom community. 1: A complete change in diatom species assemblages occurred as industrial activity commenced. 2: An apparent return to a pre-industrial (natural) estuary floras after environmental remediation. All environmental factors correlated with changes in diatom community structure with a high degree of significance yet only 31% of the variance recorded by diatom species can be accounted for by trace metal, silt and clay. Of the change in diatom species recorded through

the industrial period only 8% can reliably be accounted for. It is assumed that temporal variations in environmental factors such as salinity, pH and temperature is responsible some of the unaccounted variance.

Finally the preservation of diatom valves has improved over the time between the industrial period and the modern depositional environment. Samples from the modern estuary and from higher sections of the core, deposited after the onset of the industrial period have a higher diversity and abundance. This has occurred as organic carbon and finer grained sediments within the AHE have increased due to industrial activity, assisting in the preservation of diatom valves. Diatoms from sediment that was deposited before the industrial period are within sands and poorly preserved and therefore likely not an accurate reflection of what species were alive at the time of burial. Uncertainty in diatom preservation has implications for correctly establishing the pre-industrial (natural) baseline in order to assess subsequent change.

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1.1 INTRODUCTION

Estuaries are one of the most important and diverse ecosystems on Earth, both biologically and socioeconomically (Lotze 2010). They are critical transition zones, where land, fresh water and marine habitats are linked (Levin et al. 2001), most of which are less than 15,000 years old (Smol & Stoermer 2010). Forming sheltered habitats where terrestrial, freshwater and marine systems interact, estuaries have an abundant nutrient supply, efficient nutrient retention and effective water circulation which make them highly productive and fertile areas (Lotze 2010). In most studies estuaries are defined as a tidal coastal system where changes in inorganic salts are clearly detectable, highlighted in Pritchard (1967), "An estuary is a semi enclosed coastal body of water which has a free connection with the sea and within which sea water is measurably diluted by terrestrial fresh water". This thesis will use Pritchard's definition. Most literature accept that lagoons, fjords, river mouths and drowned river valleys also fit this description (Hume and Herdendorf 1988; Hume 2003; Smol & Stoermer 2010). Primary productivity in estuarine areas is high providing a concentrated food supply, which is able to support a diverse array of higher trophic level organisms. Estuaries tend to naturally be eutrophic habitats due to nutrient discharge via land run off (Majewska et al. 2012). Estuarine ecosystems are further enhanced by seasonal visitors, such as birds and marine organisms, which visit to feed, breed and raise their young. Another distinguishing feature of estuaries are the elevated hydrodynamics in comparison to other aquatic environments. When combined with tidal influences makes these systems exceptionally variable spatially and temporally (Wolowicz et al. 2007). Environmental factors such as water temperature, oxygen saturation, salinity, nutrient and contaminant distribution as well as diurnal and seasonal variation all create ecological stresses to local communities. It is not surprising that due to the high level of variability estuaries are often thought of being the most naturally stressful of all aquatic environments (Wolowicz et al. 2007).

Estuaries make an attractive area for human settlement, being sheltered links to the ocean and having abundant food sources. At the turn of the twentieth century, coastal areas were home to one billion people worldwide (Smol and Stoermer 2010). Of the 32 largest cities in the world, 22 are located around estuaries, in New Zealand 12% of the estuaries have a population greater than 5000 people and typically NZ estuaries have around 500 people living adjacent to their shores (Mclay 1976).

Estuaries have an extremely long and well documented history of human activity and until recently the severity to which these activities effect estuary ecosystem has both been poorly understood, and largely ignored. Now however, estuaries are considered one of the most threatened ecosystems in the word (Estuaries 2007). It is widely agreed that the natural structure and processes of estuaries have been heavily damaged by human impacts (Lotze 2010). In addition studies have shown that human activities both around an estuary, and further upstream, where potentially harmful compounds (pesticides, trace metals, dioxins) which do not disintegrate rapidly may increase ecological stress to many aquatic communities, and can be further introduced to the marine environments through this gateway (Majewska et al. 2012; Wolowicz et al. 2007).

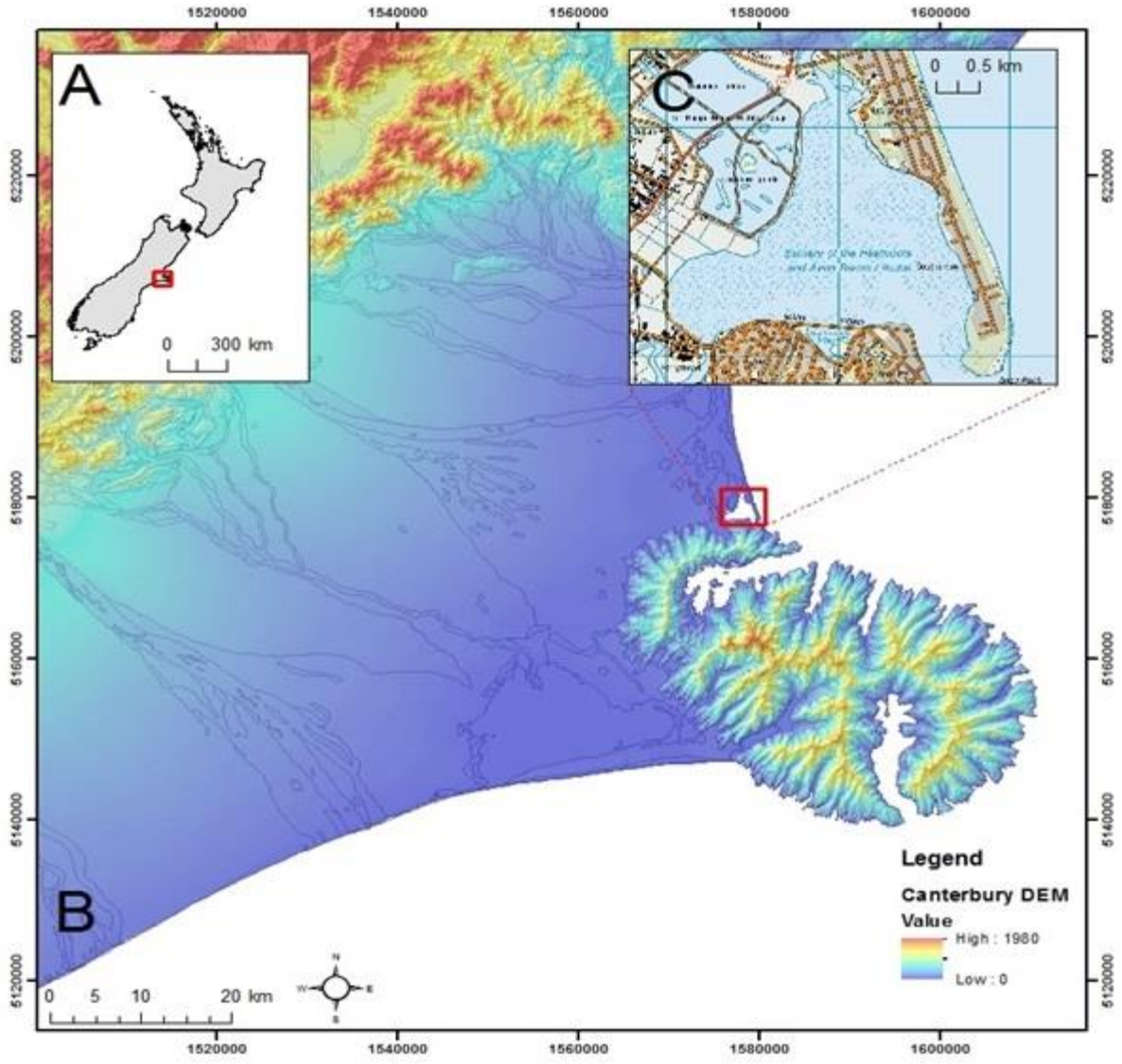


Figure 1.1: A: Map on New Zealand showing with the location of Christchurch outlined. B: Digital Elevation Map of the Canterbury plains and Port Hills, The Avon Heathcote estuary is outlined and enlarges in image C.

1.2 HISTORY OF THE AVON-HEATHCOTE ESTUARY/IHUTAI AND RIVERS

1.2.1 The Estuary

The Avon-Heathcote Estuary/Ihutai (AHE) is located in the Eastern suburbs of Christchurch City, bounded by the Miocene basalt and basaltic-andesitic volcanic complex of Banks Peninsula, and a 5km long sandy spit separating the estuary from the Pacific Ocean (Figure 1.1). It is a small, micro tidal (0-2m tidal range) estuary (Macpherson 1978), having an area of approximately 8km^2 and roughly triangular in shape. It is an area where fresh water from the Avon and Heathcote Rivers is able to mix with saline ocean water in a semi-enclosed basin forming a brackish, tidal environment (Jupp et al., 2007).

The Canterbury Plains in which the AHE is located extend from the township of Timaru to the South, to the Waipara River to the North, covering an area over 50km in width and 150km in length (Figure 1.1). These plains were progressively built during the late Quaternary via a series of glacial outwash and alluvial fan deposits. Coastline at peak transgression (6000 to 7000yBP) would place the coastline where the Christchurch suburb of Riccarton currently resides (Deely 1991). Over the last 5000 years while sea level has maintained a steady level, the rising Southern Alps, and subsequent uplift of the Canterbury plains has meant that the Pegasus Bay coastline has steadily migrated eastward leaving behind a distinctive sequence of deposits progressing from inland swamp remains to that of the modern beach (Macpherson 1978).

The Canterbury coast has hosted multiple forms of the Avon-Heathcote Estuary/Ihutai over the previous 4000 years, changing from an open bay, to estuary, to lagoon and back again. Tectonic activity is believed to be the driving force behind changes recorded in late Holocene geomorphology of the Canterbury Coast, and subsequently the AHE (McFadgen and Goff 2005). Modification of coastal geomorphology, specifically spit formation, reflects delayed alterations in sediment delivery into Canterbury river system, namely the Waimakariri River, and by extension sediment available for long-shore drift, caused by tectonic activity. Sediment load alterations can force rivers to avulse, thus large earthquakes which effect sediment load in the catchment area of the Waimakariri River can cause avulsion either north or southwards of the Waimakariri River, changing sediment supply up and down the Canterbury coastline (McFadgen and Goff 2005).

While the AHE has existed on three separate occasions, intermittently being fully enclosed or completely opened up, over the last 4000 years, its current form was formed between ~450yr BP – present. ~450yr BP the AHE was fully enclosed (McFadgen and Goff 2005). Kairaki Sands deposited on the barrier separating the AHE from the ocean allowed the AHE water level to be higher than that of the ocean, recorded as Moncks Cave was flooded during this period. The Waimakariri River, at this

time, flowed to the south, into Lake Ellesmere, thus the flow going into the AHE was insufficient to maintain an opening with the ocean (McFadgen and Goff 2005). During this period the Waimakariri River moved north and for a short period flowed directly into the AHE creating a opening in the barrier. The Waimakariri River continued migrating north until it reached its current position (McFadgen and Goff 2005).

1.2.2 Avon River

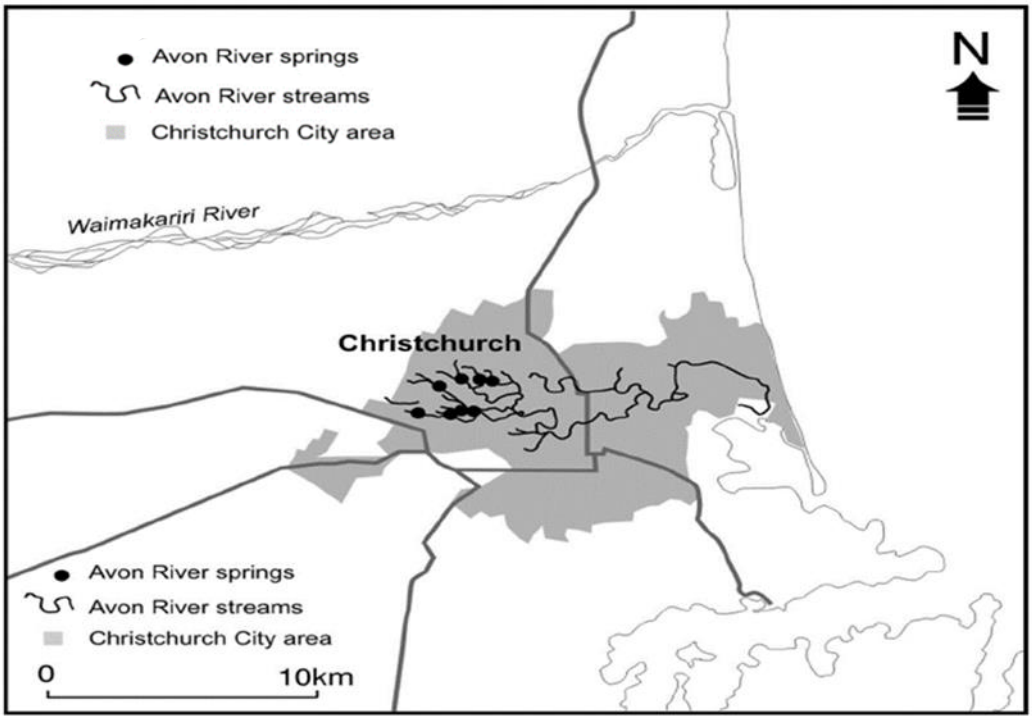
The Avon River is 26km long, is spring-fed and carries an estimated low flow of 2.7m^3/s at its point of entry to the estuary (Figure 1.2). It passes through extensive suburban areas and the central business district of Christchurch, finally draining into the northern apex of the Avon-Heathcote Estuary/Ihutai (Owen 1992). The Avon originates from multiple fresh water springs attributed to widespread aquifers beneath Christchurch and the surrounding plains. Three connecting aquifer units have been identified by (White 2009) composing the "recharge area" of the Avon River (White, 2009). The first aquifer unit known as the Harewood Floodway, located to the North East of Christchurch it is the connecting point between the entire aquifer system and the Waimakariri River. The second unit called the Fendalton gravel lobe or City gravel lobe underlies what is now the centre of Christchurch and supports almost all of the springs associated with the Avon River (White 2009). The third, final and by far the smallest unit is referred to as the Airport Floodway, which is a small gravel tongue up to 2km wide which links the Harewood Floodway and the City gravel lobe. All three of these units are palaeofloodways for the Waimakariri River, which has now been restricted by the development of Crossbank river entrainments, groins and river diversions.

Both the Waimakariri River and rainfall contribute to aquifer pressure which maintains the flow of the Avon River springs. Of the two sources recharge from the Waimakariri River is believed to be the most significant component, providing 1372 L/s out of 1697 L/s, the remaining 325 L/s is provided by local rainfall draining into the Avon River and seeping into the aquifers around Christchurch (Figure 1.3) (White 2009).

1.2.3 Heathcote River

The Heathcote River is a spring-fed meandering river, which has a total catchment of 103.4km^2 made up by a substantial portion of the Port Hill's and surrounding urban area. Only one significant tributary, the Cashmere stream, leads into it and is estimated to carry 0.38m^3/s where it drains into the Avon-Heathcote Estuary/Ihutai (south-west corner). Studies tend to focus more specifically on the origins of the Avon River with very little research being directed into anthropogenic effects which it may be subject to. The opposite is true for the Heathcote River, as it once was the central industrial

hub (Woolston) of Christchurch city, which has, in the past, been subject to high levels of industrial and organic effluent (Owen 1992) .



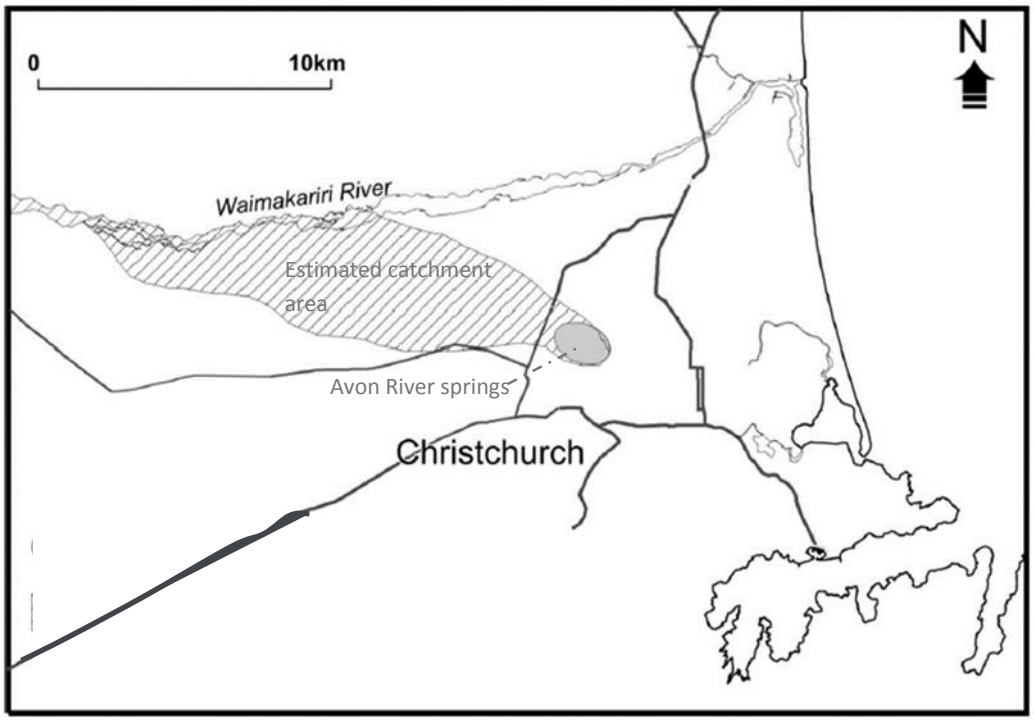


Figure 1.2 (above) & 1.3 (below): 1.3 Location of Avon River springs and streams, modified from White 2009. 1.3 Hypothesised catchment of the Avon River Springs, modified from White 2009.

1.3 HISTORY OF HUMAN SETTLEMENT AROUND THE AHE

1.3.1 Maori Settlement

The exact date of Polynesian settlement of the Canterbury area is unknown, but it is thought to be around 600-700Ybp (Penney 1982). Radiocarbon dating of pollen and organic material found in cores constrain abrupt major deforestation to the last millennium, and European explorers record deforestation had already occurred when they arrived (Challis 1995). Other potential reasons for the abrupt deforestation of the Canterbury area include periodically dryer periods in the last 3000 years making it impossible to definitively associate the 600-700Ybp deforestation with anthropogenic actives, whether they be accidental or deliberate as a method of increasing food production. It is widely accepted that forest fire frequency rose early in the millennium due to human arrival. Resulting effects of this was a notable increase in sediment load in the waterways, which filled up marshland areas and affected river mouths (Challis 1995).

Although it is estimated that no more than 500 Maori inhabited the Canterbury region pre European settlement a notable effect on the environment has been indicated. By 500Ybp, 1000's of hectares of the Canterbury plains had been deforested, resulting in a loss of many bird species such as the moa. With the loss of large avian species the estuary/marine interface became a more reliable source of food (Penney 1982) and subsequently areas such as Redcliffs and the northern bank of the AHE and river mouths were favoured sites for settlement (Challis 1995; Penney 1982).

1.3.2 European Settlement and industrialisation

Europeans first discovered the Canterbury region when Captain Cook identified Banks Peninsula in 1770, although originally mistaken as an island it was later correctly identified as a peninsula by Captain Chase in 1809. In the late 1830's European traders started purchasing land in Canterbury as a result of flourishing trade. By the 1840's European expansion was fully established in the Canterbury region, with French and German colonists arriving in Akaroa and European reclamation of the AHE margins and river banks. In 1844 a quote from one early settler, John Deans, describing the Avon River as "A river of water clearer than crystal" (Owen 1992). By 1860 water taken from the Avon River needed to be boiled before put to any practical use and at the same time industrial effluent began to be discharged into the Heathcote River (Deely 1991).

From 1860 to the early 1900's the suburbs Woolston and Sydenham were the main iron working districts and the chief industrial hubs of New Zealand. By the 1870's development was underway to drain low lying marsh areas. In 1874 the city outfall drain was developed and an increasing growth of introduced watercress (Avon) and willow (Heathcote) were noted. The invasive plants radically increasing sedimentation in river channels. By 1875, 10600 settlers were resident in Christchurch City and sources of industrial pollutants discharging into the Heathcote River included multiple wool scours, tanneries and glue factories, metal foundries and breweries (Knox & Kilner, 1973). The 1880's saw the initial development of the Bromley sewage farm (1882) and its completion in 1885 (Deely 1991). Organic waste was filtered through sand beds before being released into the AHE.

All metalled roads were introduced and the Lyttleton rail tunnel was completed through the 1880's, this development ceased any need for trade along the Heathcote River and previous work to control willow ceased also, further exasperating sedimentation problems.

Through the 1880's and up until 1925 industrial effluent was discharged into the Heathcote River, increasing by 1903 to an estimated 4.5 million litres of industrial waste daily (Owen 1992). Contributors include a starch factory, iron and brass foundries, wool scours, flax mills, limekilns and a gas works. During this period the main source of fuel used was coal and many reports from the industrial area recorded a layer of soot covering all buildings, the atmosphere being dark and murky and limited vegetation able to grow (Deely 1991). By 1926 tar was able to be produced at the Woolston gas works and roads were rapidly sealed. At this point in time effluent was still being discharged directly into tributaries of the Heathcote River with no treatment.

The types of contaminants discharged during the industrial expansion of Christchurch from 1860-1970's include arsenic and chromium (Tanneries), lead (battery factories), hydrogen chloride (glue works), acids, alkalis and sulphur (woollen mills), calcium bisulphate (wool scours), iron, copper, zinc, chromium, nickel, iron (metal works) tars and oils (gas works) and coal particles from the soot produced in making the energy to power all the for mentioned industrial works (Deely 1991; Knox and Kilner 1973).

1.3.3 Clean Up

By the start of the 1920s there was recognition of how dramatically Christchurch's development had affected both the Estuary and rivers. Active efforts to improve the quality of living for those around the AHE and associated rivers began. Multiple storm water and sewage drains were

built in outlying areas and efforts to reduce sedimentation of the Avon and Heathcote Rivers were undertaken, including controlling watercress and willow distribution, dredging and widening of both river channels (Deely 1991; Owen 1992). By the 1930s many of the industrial facilities that were prominent in the late 1800's were removed, leaving a few tanneries and iron/brass works as well as a gas-works reaming along the Heathcote River. In the late 50s and early 60s the Bromley sewage farm was expanded to the present system, by 1965 the Sumner sewage system was linked to the Bromley treatment farm (Owen 1992). The remaining starch factory (Provita) was closed down in 1968 and by 1972 all industrial effluent, excluding that produced by the gas-works, was being diverted directly to the CBD treatment plant before being discharged. The Christchurch Gas Works was finally closed down in 1981. Prior to the diversion of industrial waste 10 million litres of industrial effluent from over 150 different sources was being discharged daily into the Heathcote River.

In recent years point sources for pollution have decreased dramatically, generally restricted to urban activates such as fuel combustion, vehicle wear and trace metal's associated with building materials such as Zn and Pb from galvanized roofs and house paint. These pollutants find their way the aquatic environment via storm water runoff (Nipper et al. 1997). Large areas of the AHE are still enriched in trace metals with the finer sediments around the Avon and Heathcote River mouths containing the highest concentrations presently (Deely 1991).

Resulting metal concentration are greatest in estuarine sediments deposited post European settlement, when sedimentation rates are at their slowest. The lowest trace metal concentrations are found in sediments that are rapidly deposited and in sediment formed pre-European settlement. Significant trace metal pollution has entered the estuary since 1850 as a direct result of anthropogenic activities, additionally the concentration distributions have been modified by variations in sedimentation rates, which were in turn determined by changes in land use and drainage of the surrounding Canterbury area (Deely and Fergusson 1994).

1.4 DIATOMS

1.4.1 Biology

Diatoms (Class Bacillariophyceae) are unicellular, eukaryotic, microscopic algae found as free cells, colonies, chains, or attached to a substrate. Diatoms are comprised largely of biogenic silica ($SiO_2.nH_2O$) with a thin organic coating, which enclose the eukaryotic protoplast (Seckback and Kociolek 2011). Most are pigmented and photosynthetic and some species are able to survive heterotrophically if supplied with sufficient organic carbon (Round et al. 1990). Diatom are quite often a dominant component of benthic microalgal assemblages (Sullivan and Trobajo 2010) in estuarine

environments. A complete frustule (full diatom) comprises of two relatively larger components (valves), each with an associated series of bands (the girdle or cingulum) (Figure 1.4), the older valve and its cingulum being termed the epitheca is the larger of the two, while the younger set is termed hypotheca and fits snugly inside the older valve (Figure 1.4). Diatoms primarily reproduce by mitotic division, with infrequent sexual events (Armbrust 2009), thus during cell division each offspring inherits one half of the parent wall, but must also synthesize a new half wall (hypotheca) and cingulum before full separation occurs. Older epitheca can potentially exist for many cycles. Successive sexual mototic reproduction produce smaller valves, sexual reproduction phases produce full sized valves. Most range between 0.005 – 0.1mm in size, meaning individual cells can only be observed under microscope analysis. Diatoms can only be seen with the naked eye when growing in large numbers,

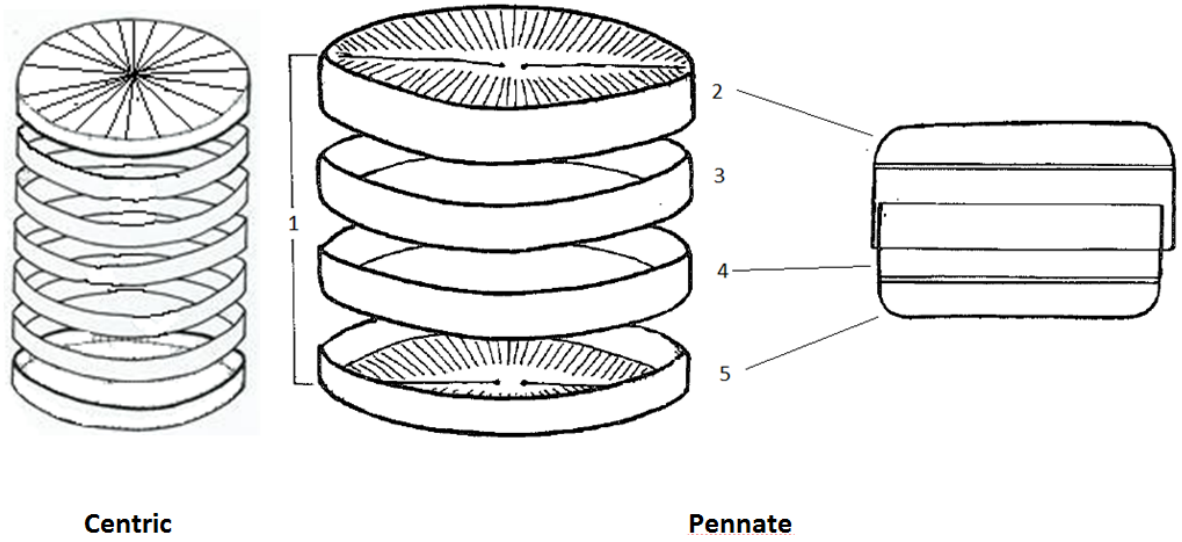


Figure 1.4: Centric and Pennate diatom cell wall structure, 1: Basic components of a diatom, 2: Epivalve, 3: Epicingulum, 4: Hypocingulum, 5: Hypovalve. Modified from (Barber & Haworth, 1994)

such as ocean algal blooms, slime on rocks and river beds and in puddles. A well-known introduced example of a diatom in New Zealand is *Didymosphenia germinata* otherwise known as Dydimo or Rock snot, first identified in 2004, which has an adverse effect on fish, invertebrate habitats and biodiversity of South Island New Zealand streams.

Diatom habit is generally grouped into planktonic (open waters) and benthic (lake and ocean floor). Planktonic diatoms can be treated as separate entities suspended in the water column, benthic diatoms on the other hand can be split into four sub groups (epipsammic, epipelic, epilithic and epiphytic) based on distinct micro-environments within the sediment interface (Young 2010).

Epipsammic algae live attached to grains in sandy sediments (Figure 1.5), attaching themselves to individual grains by mucilage or stalks, preferably in relatively stable sediment (Moss

1977; Round 1981). Epipsammic forms are often non-mobile or if they are motile they are generally slow moving. In the event that they are buried by wave action of animal disturbance they are able to tolerate both darkness and anaerobic conditions for extended periods of time.

Epipelic diatoms live freely on the sediment surface (Moss 1977) and are generally large and motile (Figure 1.5). Epipelic diatoms are tolerant of darkness for extended period of time, but not of anaerobiosis. As they live in a dynamic environment where burial via wave action or burrowing organisms is common, as is the threat of predation from grazing micro-organisms they must rely on their rapid movement to retain their position on the sediment surface (Young 2010).

Epilithic diatoms differ from other benthic diatoms by encrusting rocks or other hard substrates that are larger than the diatom (Figure 1.5) (Young 2010). This ability allows epilithic diatoms to feed on surrounding organic matter and nutrients for growth (Young 2010).

Epiphytic diatoms attach themselves to other larger algae and are added by the potential motility of their selected host. This lifestyle grants epiphytic diatoms access to sources of nutrients whilst being attached to the larger algae or plant, the drawback to this lifestyle is that epiphytic diatoms are more likely to be subjected to grazing than other diatoms.

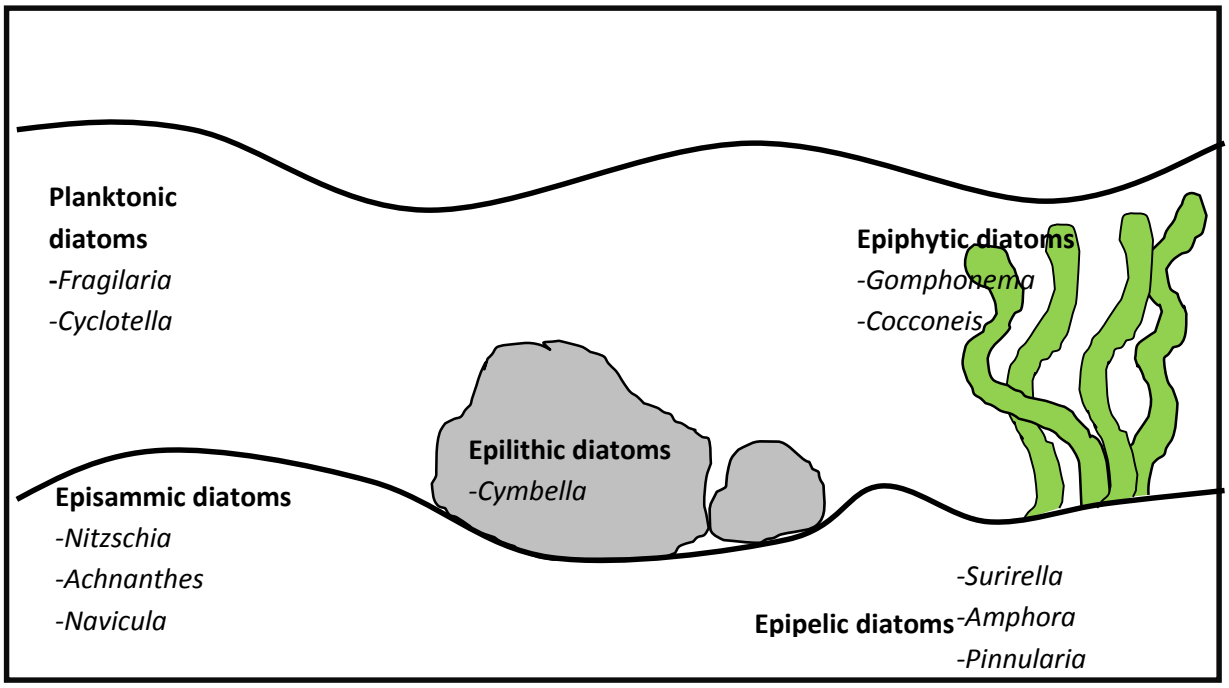


Figure 1.5: Habitat areas of living diatoms, modified from Young 2010.

Diatoms have been well established since the early Jurassic (170Mya) (Round et al. 1990) and are estimated to have arose as early as 250Mys (Armbrust 2009). Armbrust (2009) and Seckbach and Kociolek (2011) estiamte that diatoms originated in the Triassic around 250Mya. Early diatoms are highly silicified and radial centric in shape, initially been restricted to a near shore benthic lifestyle. Recent studies indicate that the highly silicate walls may be a response to a terrestrial heritage, where the ability to metabolize silica could have evolved to help protect against desiccation (Seckback & Kociolek, 2011). At ~100Mya a second divergence occurred, where the first bipolar and multipolar centric forms are recorded. Around 65Mya the Cretaceous extinction, where about 85% of all life forms on Earth were lost. The K/T extinction event had relatively little effect on diatoms, perhaps leaving large un-occupied environments for diatoms to expand into allowing for the third diversification, the araphid pennate to become established (Armbrust 2009). At 30Mya the fourth major branch of diatoms immerged, the raphid diatoms, with the ability to actively move (Armbrust 2009), giving way to another substantial period of diversification as even more niches became available.

1.4.2 Applications of diatom in environmental science

Diatoms are extremely well suited for studies of environmental change and paleoenvironmental reconstruction due to some key characteristics:

1. Highly abundant in most environments.
2. Have a rapid reproduction rate.
3. Are sensitive to a wide range of environmental factors.
4. Respond quickly to changes in water conditions.
5. Can be accurately identified by the shape, size and sculpting.
6. They preserve well, and are usually present in high abundance in lake and estuarine deposits.

Palaeoecologists are able to group species according to habitat, salinity, pH, nutrient content, water depth/moisture, oxygen requirements and various other environmental factors (Cochran 2002). This means that by analysing changes between diatom communities as well as within individual communities, the effect of environmental influences can be identified.

Originally diatoms were collected for fashion and as a standard for microscope development. In scientific analysis diatoms were originally used to track isostatic rebound in Scandinavia and more recently diatoms have been used to help with the determination of lake acidification is a natural or

anthropogenic process. Modern diatom studies in estuarine environments include analysing spatial and temporal distributions to determine what environmental pressures explain them, including but not limited to Admiraal (1977); Admiraal and Peletier (1980); Haynes et al. (2011); Majewska et al. (2012); Rovira et al. (2009); Saunders (2011) and Schowe et al. (2012). Additionally effects of common industrial pollutants such as trace metals on diatom communities and individual cells have also been studied (Augustinus et al. 2006; Cattaneo et al. 2008; Ferreira da Silva et al. 2009; Medley and Clements 2011; Tadros et al. 1990).

1.5 PREVIOUS DIATOM WORK IN NEW ZEALAND

New Zealand's history of diatom research has been rather short, initially starting with diatom collecting in the 1850's to create artistic collection pieces. The first actual collections for scientific purposes in New Zealand were undertaken by Dr W Launder Lindsy, who collected diatoms from swamps, lagoons, ravines and various rock faces around the Otago region. Multiple checklists have been created including Crosby and Wood (1958) and Wood (1961), further expanded by Foged (1979) who sampled extensively from a wide range of habitats in the North Island. More recently a complete checklist of previous work can be found in Cassie (1984). Marine diatom checklists are more exclusive in New Zealand, as are and focused studies on diatoms, two of the more important lists are Stidolph (1980) and Taylor (1970).

Aside from general checklists and species collection lists, New Zealand diatom studies have gravitated, at least in the fresh water realm, to those that can be used to study environmental change. Diatom floras have been used to indicate that Wellington is built on old lake mud (Begg et al. 1993). Cochran et al. (1999) using diatoms were able to show a transition from lake to marine environments in Lake Kohangapiripiri, Wellington, as well as showing that the seismic process which facilitated that change. Further studies used to constrain geological events include Harper et al. (1986) where diatom blooms in Lake Poukawa was seen to follow volcanic eruptions.

The anthropogenic effects on the environment have also been studied using diatom flora in New Zealand. Recent studies include Schowe et al. (2013), where the community response of freshwater diatoms were studied under the effects of Acid Mining Draining (AMD). Thirty nine streams were studied along an AMD gradient. The taxonomic richness was greatly reduced in severely impacted streams, but it was noted that diatoms which originated from a slightly acidic environment were better able to tolerate moderate conductivity and metal concentrations. Schallenberg et al. (2012) successfully used diatoms along with other environmental factors to determine

palaeoenvironmental changes, which included marine inundation and mass conversion from natural wilderness to productive agricultural lands in East coast lakes in the South Island from the start of the Holocene through to present day. Augustinus et al. (2006) successfully used diatom flora to study the anthropogenic impacts caused by the urbanisation of Auckland City around Lake Pupuke, reporting changes in diatom assemblages, trace metal spikes and distinct sedimentological alterations.

There has been limited analysis of assemblage composition and environmental factors influencing distribution of New Zealand diatoms. What little has been done is restricted to mainly a fresh water (Cassie 1984), marine or invasive introduced species such as *Didymosphenia geminate* or "Didymo" (Kilroy and Unwin 2011). Estuarine diatom studies are extremely rare, McClatchie et al. (1982) if one of the few, which looks at the community composition of a single locality in the AHE and how diatom communities are effected by predation. Few studies in New Zealand have attempted to determine the temporal and spatial effects of trace metals, sediment size and nutrient concentration, on diatom communities and general species distribution.

1.6 ENVIRONMENTAL AND ANTHROPOGENIC INFLUENCES

1.6.1 Trace metals

Arsenic can usually be detected in metamorphic and sedimentary rocks at low concentration, in New Zealand arsenic has historically had a major role as a preservative in the timber industry (copper chrome arsenic) and due to this is a well-recognized contaminant. Lead arsenate was commonly used as historic pesticide, which can be introduced into the AHE if used within the catchment area. Additionally recordable levels of arsenic are found on street surfaces, likely from brake pads, tires and in bitumen (Environment Canterbury, 2012).

Cadmium sources in New Zealand include brake pads and linings as well as tires (Kennedy and Gadd, 2000). Other sources which can be found in urban environments include batteries, pigments, coatings and plating, stabilizers for plastics, alloys and smelting.

Chromium sources are common in urban environments, being used in treating timber (in copper chrome arsenic) as well as being incorporated in paints, plating and the bodywork of vehicles. Kennedy and Gadd (2000) conclude chromium is in many motor vehicle emissions as well as dust created via wearing on brake pads. Within Christchurch specifically multiple studies have been undertaken which present data for chromium in street surface dust and materials used in commercial lands (Fergusson and Ryan 1984; Fergusson and Simmonds 1983).

Cobalt is a naturally distributed trace metal occurring in rocks, soils water and vegetation, always occurring in nature in association with nickel and sometimes arsenic. Industrial sources of cobalt occur when arsenical ores of nickel, copper and lead are smelted (Domingo 1989).

Copper is an extremely common metal used in all manner of urban building materials (pipes, wiring and guttering) additionally it has been widely used in the forestry industry as a component of copper chrome arsenic. Kennedy and Gadd (2000) identified copper's inclusion in brake pad formation as a key source of copper in urban environments while other documented sources include motor vehicle related discharges and agricultural herbicides.

Lead is a known contaminant in urban environments, historically being used in building paints, leaded petrol and lead based industries and can be commonly found in house flashings. Recorded levels of lead from periods when leaded petrol were in common use show that concentrations of Pb were extremely high, contribution to more than 90% of the total lead emitted to the environment (Golder 2012) but since the abandonment of leaded petrol the average of lead has fallen below 200mg/kg in whole dust (Golder 2012).

Manganese has been found in a variety of industries, crafts, and agricultural activities due to its physical and chemical properties, sources include smelter emissions and waste sewage in water. Further, organic compounds of manganese have been used as a antiknock substance in gasoline (Shukla and Singhal 1984).

Nickel sources include steel, electronics and batteries as well as household appliances, although it is common it still is not as common as trace metals such as copper or zinc. Fergusson and Simmonds (1983) reported a mean nickel concentration of 19.9mg/kg in dusts collected from gutters in Christchurch, which was similar to the mean concentration recorded in Wellington by Kennnedy (2003).

Zinc has had extensive use in paint, rubber and the galvanising of materials as well as tyres and brake pads. Many studies have been undertaken on particulate material found on road surfaces (Median concentration 482mg/kg) in Fergusson and Simmonds (1983) which is mirrored studies taken in wider New Zealand (Kennedy and Gadd, 2002; Ng et al. 2003).

1.6.2 Organics

Organics have been selected for measurement for two reasons, 1) to see if it has any recordable effect on diatom abundance, diversity or distribution and 2) the amount of organic matter in samples can influence the concentration of trace metals. Metals such as copper will use organic

material as sites for sorption which can assist in increasing copper concentrations. Other elements can be effected in the opposite manner with organic matter acting as a diluent (Golder 2012).

1.7 PURPOSE OF RESEARCH

In order to establish ecosystem health, and accurately predict possible future changes and their effect on estuaries a comprehensive understanding of estuaries natural levels of organic content, trace metals and diatom assemblages, prior to human influence, as well as how much change has occurred as a direct result of human interference must be understood. This study aims to establish the composition of diatom species in the AHE prior to human settlement, and the associated effects human activities have had on diatoms to the present day.

1.7.1 Research Aims

1. Understand the distribution of modern Bacillariophyceae (diatom) assemblages in response to habitat, substrate, salinity, pH and trace metal concentration in the Avon-Heathcote Estuary/Ihutai.
2. Develop a record of historic and pre-historic diatoms in the Avon-Heathcote Estuary/Ihutai and establish the species composition and diversity of the Avon-Heathcote Estuary/Ihutai prior to human settlement.
3. Use the pre-historic diatom record to describe how the estuary has changed over the last 150 years and improve the understanding of what factors have contributed to that change.
4. Identify and record of historic or pre-historic seismic difference in the AHE.

This thesis will assess any potential effects of human activities on the diversity and abundance of diatoms, an important group of primary producers in the AHE.

CHAPTER TWO - METHODS

2.1 SCOPE OF CHAPTER

This chapter outlines methods used to collect and process both modern and ancient sediment samples retrieved from the AHE. The content of this chapter has been divided into two encompassing sections, field techniques (Section 2.2) and laboratory techniques (Section 2.3). Many of the techniques used in this project have been successfully implemented in other studies and thus some procedures are similar to those outlined in (Cochran 2002).

2.2 FIELD TECHNIQUES

2.2.1 Site Selection

Sample collection sites were selected to record the full tidal range covering a combination of plant zones and sediment sizes. Multiple sites were selected throughout the estuary to capture variation in trace metal and organic carbon concentrations from the edges of the Avon and Heathcote River mouths to the estuary/ocean interface. The five sampling locations were

1) Bridge St
2) Western edge of Southshore Spit
3) Moncks Bay
4) McCormacks Bay
5) Settlers Crescent

Each site was divided into zones that reflect tidal height. These zones begin above maximum spring tide (Z+2) and extend to maximum low tide (Z5) allowing tidal exposure to be assessed in relation to diatom distribution.

2.2.2 Modern Diatom Sample Collection

At each site one plastic non-reactive bag was half filled with sediment collected from the top centimetre of the surface. An aluminium trowel was used when collecting sediment as it is non-reactive. Between each collection the trowel was cleaned to ensure no cross contamination occurred. Sites were mapped using Trimble R8 GNSS GPS equipment, which were sited in reference to geodetic marker A572 (Avon River mouth) to zero in GPS.

After sampling at each field location, samples were returned to the University of Canterbury's sedimentology lab in the Geological Sciences Department and split into four separate units; three

small sediment samples for trace metal analysis, grain size analysis and diatom processing respectively, while the remaining sediment was stored in the geological fridges in case any additional tests were required and was subsequently used for Caesium dating.

2.2.3 Live Diatom Sampling

Sampling of live diatoms occurred at the Bridge St sampling site, live diatom samples were collected at BSZ4. Sampling of live diatoms consisted of storing both surface sediment and estuarine water from the sampling site in a nonreactive plastic container, sediment was extracted using a stainless steel trowel while water was scoped directly into a storage vessel. Collected samples were transported to the University of Canterbury's sedimentology lab in the Geological department for processing and storage.

2.2.3 Environmental Sampling

Salinity, pH, conductivity and water temperature around the AHE were recorded using a handheld HACH multimeter. Each of these factors were sampled at the lowest sample site on each transect, in estuarine water or running river water when possible. Ponded water, defined as water which was trapped in channels are the tide receded, was also sampled when possible.

2.2.4 Coring

The coring location was selected to as a site with continuous sedimentation and in proximity to a site with interpreted coseismic deformation shown by foraminifera (Hayward et al, in prep 2014). A sediment core was collected using a Eijkelkamp gouge auger (EGA), which has multiple semi-cylindrical chambers and barrel length of 100cm. For this study two separate chambers with a diameter of 6cm and 2cm were used. The EGA samples sediment by pushing a chamber into undisturbed sediment, then rotating and retracting the barrel out of the sediment. Additional extension rods between the sampler and a T-bar handle enables successive depths to be collected, thus continuous sampling can be achieved through careful measurement of depth of penetration at each stage. At each site the EGA was operated by two people and coring continued until further penetration of sediment became impossible. Sediment sections extracted from the EGA were wrapped in plastic, labelled and placed in PVC downpipe tubing for transport and storage.

Each EGA core section was logged in the University of Canterbury Geological Sciences sedimentary lab. Every 10cm, 2cm of sediment was subsampled from each core for diatom, trace metal, organic and grain size analysis. The removed sections of core were replaced by wooden chocks

to maintain the correct core length and keep the remaining sediment separated (Figure 2.1). A total of 30 subsamples were collected. Remaining cores are stored in the University of Canterbury's Geological Sciences Department.

Figure 2.1: Three sections of the Bridge St core with wooden chocks used to replace sediment taken for analysis.

2.3 LABORATORY TECHNIQUES

2.3.1 Diatom Processing

Live diatom samples were placed into a petri dish and then overlaid with extremely fine filter paper. The filter paper was allowed to rest inside the petri dish, in contact with sediment and for 24 hours in a sunny area of the lab. Additional estuarine water was added when needed as evaporation occurred. The filter paper acted as a trap for live diatom as they attempt to travel toward the source of light. After the allotted time had elapsed the filter paper was removed and dissolved in hydrogen peroxide and then live diatom samples were processed using the same steps as all other samples collected from the AHE.

Processing sediment samples for diatom valves was undertaken with 20-30 samples at a time using procedures similar to those outlined in Battarbee (1973) and Cochran (2002). Initially 1gm of sample was weighed out and left to dry over night at 70^{o}C in a clean 50ml glass beaker. Samples were then covered with 20ml of 27% hydrogen peroxide and left overnight to digest any organic matter present. Samples consisting of completely organic material (plant samples) were left for two to three days, periodically topping up the level of hydrogen peroxide until all organic material was fully digested. Carbonate material was removed by adding 10 ml of 32% hydrochloric acid slowly to the remaining solution of each sample. Vigorously reacting samples were left until reactions ceased.

Samples were then heated until visible reactions ceased then additional HCL was added to confirm no further reaction occurred. Samples were transferred into 50 ml plastic centrifuge tubes and rinsed with distilled water. Filtered water was added to digested samples and centrifuged at 3000 revolutions per minute (rpm) for five minutes. Fluids were decanted off and tubes refilled with deionized H_2O; this process was repeated until samples were a clear colour, indicating that all acid had been removed.

Sand was removed from each sample by suspending sediment in 45 ml of filtered water in a centrifuge tube, each tube was shaken for 15 seconds and allowed to settle, after which solution the was poured off into a new tube. Diatoms are generally smaller than sand grains and should be suspended in the shaken solution. Sediment remaining in the original tube was set aside and stored. The shaking and settling process was repeated so samples ended up in their original tubes. This process was repeated until the majority of sand sized grains were removed, following Cochran (2002).

Clay was removed by re-suspending samples in filtered water with six drops of dilute sodium hexa-metaphosphate (calgon), shaken and then centrifuging at 1800 rpm for three minutes. The cloudy solution was discarded, the tubes refilled with filtered water, shaken and centrifuged and the process repeated until the solution became clear. This took between two and ten washes. An additional wash with centrifuging at 3000 rpm for five minutes was done at the end to ensure the sample was clean, as described by Cochran 2002. Excess water was removed by pipette until only 10ml remained.

To prepare diatom slides the pipette method from Cochran (2002) was used. For each sample one microscope slide and two coverslips were warmed on a hotplate. Each sample was shaken vigorously for 30 seconds and then a drop was pipetted onto one of the two cover slips, the second cover slip received two drops of the sample. Equal volumes of lycopodium spores (suspended in 20ml of water) were added to each cover slip, each slip was then diluted with filtered water until the entire coverslip was covered. Slips were heated until the suspension evaporates off and two drops of naphrax were placed on the microscope slide and warmed also. Each cover slip was then inverted onto the naphrax drops and left to heat gently for several minutes to remove the toluene from the naphrax. Each slide was then removed and allowed to cool, bubbles were removed by gently tapping coverslips with a toothpick. Once the naphrax had hardened, excess adhesive was removed using a sharp knife and the edges were sealed with base coat, colourless nail polish. Slides were labelled and stored for identification of diatoms.

2.3.2 Trace Metal Analysis

30gm from each core and sediment sample was measured out for each site and placed into small aluminium baking trays. To ensure that the sample was accurately represented, each sample were subsampled from multiple areas. Each whole sample was then kept at 70^{o}c for a minimum of 72 hours to destroy any contaminants. Baked samples were double bagged, rolled and then sieved through a 2mm sieve to remove excessively large material (organics/shell material) and then stored in non-reactive plastic sample jars.

Sediments were prepares for ICM-MS analysis using a modification of USCPA 200.8 (Creed et al. 1994). One gram of dried sediment was weighed out and placed into acid washed digestion tubes, 4ml of (1+1) $HN0_3$ and (1+4) 10ml of HCl was added to each sample. Samples were then placed in an aluminium heating block and warmed to 85^{o}c and left to reflux for 30 minutes. The digested samples were coded and made up to 20ml using ultrapure water. Samples were diluted 21X using 2% HNO_3. ICP-MS (Agilent 7500cx) analysis quality control measures included the analysis of blank digests and a marine sediment certified reference material, mean recoveries for replicates are provided in table 2.1, and three replicates were used. To check the quality of results duplicates were included in this process, along with one triplicate to be used as a spiked sample. Certified marine sediment reference material (U.S National Institute of Standards and Technology Standard Reference Material 2702) and blanks were included in each batch digested to ensure that ICP-MS instrument was working correctly. Detection limits for desired trace metals are Cd – 0.1µgL^{-1}, As, Cu, Pb, Zn, Ni and Mn are 1.0µgL^{-1} and Fe is 4µgL^{-1} IPC-MS testing was overseen by Rob Stainthorpe of the Chemistry Department.

Table 2.1: Mean recoveries for certified reference material.

	Mean recoveries
Cr	67.97426
Mn	87.65035
Fe	65.94586
Co	76.04266
Ni	57.70746
Cu	83.48471
Zn	83.50094
As	84.34185
Cd	97.84414
Pb	92.18918

2.4.3 Pollution Indexes

Pollution indexes were created in order to establish a simplified method of determining how trace metals occurred both spatially and temporally. The Pollution Load Index (PLI) was originally developed to determine the pollutants in mussels in coastal waters. By standardizing the data using quotients (Cf) (equation 1) obtained by dividing each concentration by a baseline concentration for each chemical, in the case of Tomlinson this means the lowest concentration of each chemical found in mussels sampled and in literature. Once the Cf of each metal has been calculated the PLI is derived by calculating the n-root from the n-CFs that were obtained from each metal (equation 2). The equations from Tomlinson et al (1980) are as follows.

$$Cf = (C_{metal} / C_{baseline}) \quad (1)$$

$$PLI = \sqrt[n]{(Cf_1 \times Cf_2 \times \ldots \times Cf_n)} \quad (2)$$

The method developed by Tomlinson is effective in creating a pollution load index tailored specifically for the AHE which can then be compared to environmental factors and diatom assemblages.

Additionally to compare the total content of metals at the different sampling sites the Metal Pollution Index (MPI) was used, obtained with the equation used successfully in the paper (Usero et al. 2005) (equation 3).

$$MPI = (Cf_1 \times Cf_2 \ldots Cf_n)^{1/2} \quad (3)$$

Where Cf_i = the concentration factor for the metal (*i*) in the sample. Additionally for redundancy measures a second pollution index has been used.

Another index used to simplify comparison of trace metal results in the AHE is the Modified Degree of Contamination (mC_d) proposed initially in Hakanson (1980), where an overall indicator of contamination based on data for a series of trace metals. This index has been modified and been implemented successfully by Abrahim and Parker (2008) in New Zealand's Tamaki Estuary. Surface samples are averaged to produce a mean pollution concentration that can then be compared to a baseline "pristine" reference level, in the case of this study the base line reference has been created from trace metal data taken from our own core, at a depth which reflects an environmental period pre-dating both European and Maori influence. To calculate the mean concentration the following equation has been used (equation 4).

$$C_f = M_x / M_b \quad (4)$$

M_x refers to the mean concentration of a pollutant in the contaminated sediments while M_b refers to sediments which predate human influence (Baseline). While Hakanson continues to calculate C_d, which unfortunately is a complicated, and limited way to measure overall contamination in surface layers, this study instead adopts the modified formula presented in Abrahim and Parker (2008) (equation 5). This formula is generalized by defining the degree of contamination (mC_d) as the sum of all contamination factors (C_f) for a given set of pollutants, divided by the number of analysed pollutants. The equation to calculate the mC_d is as follows:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (5)$$

where *n* = number of analysed elements, *i* = ith element and C_f = Contamination factor.

2.3.3 Grain Size Analysis

Grain size analysis was undertaken using the Saturn digitizer II 5205 Laser Diffraction Spectrophotometer in the University of Canterbury's Geological Sciences Department. Roughly 50gm of sediment was removed from each original sample and stored in non-reactive plastic containers. To ensure samples were representative grain-size samples were taken evenly from throughout the entire original sample. Electronic reports provided the percentage of specific sediment sized grains in analysed samples, those falling below 3.9µm were classed as clays and sediments with a grain size between 62.5 µm and 3.9µm were classed as silt and those above 62.5µm as sand.

2.3.4 Organic Analysis

All stable isotopic analyses were performed in the University of Canterbury Stable Isotope Analytical Facility housed in the Department of Geological Sciences. Carbonate oxygen and carbon isotope analysis were performed using a modified version of the technique described by McCrea (1950) in the Stable Isotope Biogeochemistry Laboratory at the University of Canterbury. Between 150 to 300µg of sediment was sampled from the Avon-Heathcote estuary and then reacted at 70^{o}C with 100 percent phosphoric acid in sealed reaction vessels flushed with helium gas. Headspace sampling of evolved carbon dioxide was performed with a Finnigan Gas-Bench II and isotopic rations measured on a Finnigan Delta V+ mass spectrometer. Precision of the carbonate isotopic data is ±0.2 permil for both oxygen and carbon isotope ratios based on repeated analysis of NBS-18 and NBS-19 carbon standards, and ERCK internal carbonate standard.

2.3.5 Caesium Dating

Six samples were held at 60°C for three days to dry and then ground into a fine powder using a mortar and pestle before being stored in nonreactive containers. Samples were sent to the cosmogenic isotope and radiochemistry laboratories in GNS Science, Wellington, New Zealand.

2.4 DIATOM ANALYSIS

2.4.1 Identification

Diatom identification was carried out using an x700-1000 magnification Zeiss Photo Microscope III with differential interference contrast capabilities. Initial observations were drawn, measurements of valve length, width and shape, as well as variations in ornamentation such as striae, puncta and fibula were used for identification. These observations were then compared to Kelly et al. (2005), Krammer and Lange-Bertalot (1986; 1988; 1991a; 1991b), Lange-Bertalot (1993), Spaulding et al. (n.d.) and Witkowski et al. (2000). These are then compared to multiple New Zealand species checklist to determine that these species are present. Images were taken for each new species in order to re-check identification if needed.

2.4.2 Counting

Transects were established along each slide to avoid doubling up when counting diatom valves. Valves were only counted when over half of a single valve was present, with distinguishable identifiable features. Each modern sample was counted to a maximum of 300 valves when possible, and a minimum of 100 valves. For core slides a maximum of 100 valves were counted when possible. Due to low diatom abundance in core samples 100 valves was not always reached.

2.5 STATISTICAL ANALYSIS

2.5.1 Cluster Analysis

Cluster analysis is a method of grouping data where data that is more similar to each other is grouped together to aid in identifying trends or patterns. To develop cluster analysis PAST statistical software using Bray-Curtis weighting was used after normalizing diatom data and removing species which made up less than three percent of the total diatom valves counted. Cluster analysis was used in analysis the results of both modern and core diatom data, grouping individual diatom species into diatom “assemblages” and sample site into site “groups”. All diatom species identified that individually made up more that 3% of the total data set for either the modern setting or the core were used in these cluster analysis while species that made up less than 3% were removed from the analysis. Sites which had recorded diatom identification were used and those with no diatom present were removed before the cluster analysis was applied.

2.5.2 Spearman's rank coefficient

Spearman's rank coefficient was implemented in Microsoft office excel (2013) using initially the RANK function followed by the CORREL function with is standard in excel software. Spearman's is used multiple times both in chapter three and chapter four to establish correlations between environmental factors in order to determine if they are influencing each other as well as between environmental factors and assemblages (as defined by cluster analysis). Environmental factors included in environmental vs environmental correlations include all pollution indexes, sand, silt and clay, organic carbon concentration, sample site elevation (for modern setting) and each individual trace metal analysed in this study. For environmental factors vs diatom assemblage correlations both in the modern and core, all assemblages were used and environmental factors consisted of PLI, MPI, mCd, sediment composition, organic carbon and in the modern setting elevation.

2.5.3 Kruskal-Wallis

Kruskal-Wallis one-way analysis of variance was carried out using R statistical software. Kruskal-Wallis analysis was used in both results sections for this thesis, applied to determine differences in diatom communities across the AHE between transects as well as within each, additionally diatom data was split into elevation groupings. Furthermore environmental data was analysed the same way to identify changes in concentrations of MPI, silt, clay, organic carbon and elevation between transects in the modern setting. With data sourced from core samples both diatom and environmental data (MPI, silt, clay and carbon) were split into three groups representing the modern estuary, industrial estuary and the natural estuary before European influences arrived to determine if significantly different. Kruskal-Wallis analysis preformed in this thesis will have a alpha level (α) of 0.05. To determine if the null hypothesis (no difference) can be rejected the analysis results must be higher than the critical value. Each critical value is different depending on how many degrees of freedom (df) the analysis has, df is calculated using the following equation 6 where k is the number of groups being analysed.

$$df = k - 1 \qquad (6)$$

Using a chi^2 table (Table 2.2) a Kruskal-Wallis test with two degrees of freedom would have a critical value of 5.99. If the result of the Kruskal-Wallis analysis is higher than 5.99 than the null hypothesis can be rejected, meaning that the groups of data analysed are statistically different.

Table 2.2: Chi^2 table to determine critical value in Kruskal-Wallis analysis.

	Alpha (α)		
df	0.05	0.01	0.00
1	3.94	6.63	10.83
2	5.99	9.21	13.82
3	7.81	11.34	16.27
4	9.49	19.28	18.47
5	11.07	15.09	20.52
6	12.59	16.81	22.46

2.5.4 Two tailed t-test with unequal variance

Two tailed t-tests with unequal variance were used to determine if two sets of data differ significantly from each other, for example data sets such individual trace metals concentrations or differences between modern and historic diatom communities.

2.5.4 Canonical correspondence analysis

Canonical Correspondence Analysis (CCA) is a multivariate constrained ordination technique used to establish gradients between combinations of variable in dataset. Using R statistical software, a free to use statistical program CCA was undertaken using vegan statistical package. CCA was undertaken on data sets developed from both the modern estuary (Chapter 3) and coring (Chapter 4) to determine any relationships between diatom species and environmental factors. Three separate CCA were used in chapter 3, environmental variables for each analysis were consistent, composed of MPI, silt, clay, organic carbon in sample and elevation while assemblage data varied between each CCA. Individual CCA differed with one encompassing all diatom species, a second grouping diatom species into assemblages, as defined by cluster analysis and a third including only assemblages showing a significant change across the estuary, as defined by Kruskal-Wallis analysis. Chapter four followed the same format as chapter three, with the exclusion of elevation data from environmental parameters.

CHAPTER THREE – MODERN RESULTS

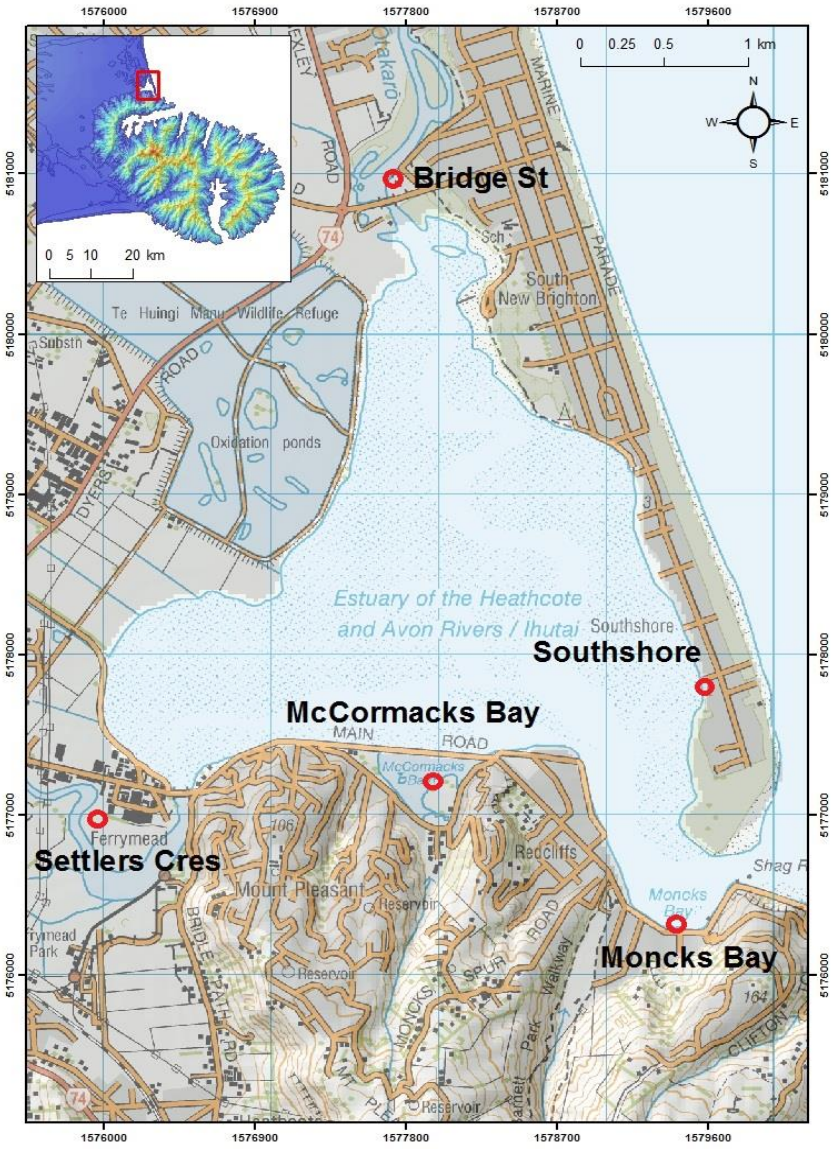


Figure 3.1: Map of sampling locations around Avon-Heathcote Estuary/Ihutai, Christchurch

3.1 INTRODUCTION

A key objective for this thesis is to understand the current distribution of modern diatoms in the AHE. This chapter will present the results of modern sampling in the AHE. Data collected includes salinity, tidal height, substrate composition, diatom composition, sediment trace metal concentration, pH levels, organic carbon concentration and diatom communities. To establish the level of influence each environmental factor has in controlling modern diatom distribution and abundance statistical methods such as cluster analysis, Spearman's rank correlation coefficient, Kruskal-Wallis one-way analysis of variance and canonical correspondence analysis were used. The methods used for sample collection are outlined in chapter two, while raw data used in this chapter are presented in Appendix A-D.

3.2 SITE DESCRIPTIONS

As described in chapter two five transect locations were chosen to study environmental factors and diatom communities. The five locations were Bridge Street, Settlers Crescent, McCormacks Bay, Southshore and Moncks Bay (Figure 3.1). Each transect was sub sampled to cover elevation changes, ranging from maximum high tide zone to maximum low tide zone.

3.2.1 Bridge Street

The Bridge St transect (BS) is nestled between a small vegetated parkland and the Avon River, on the northern side of the Bridge Street bridge (Figure 3.2). At low tide the sample location consists of grassy berms, tidal mudflats with intermittent channels, dense jointed sedge thickets and areas of glasswort. The distribution of Sarcocornia, jointed sedge, grass and flax is in flux as the area is now periodically inundated by estuarine tidal water due to 0.2 to 0.5m of subsidence caused by the February 2011 Christchurch earthquakes (Measures et al. 2011; C M Reid et al. 2013). Evidence of subsidence can be seen where upper areas of the reserve, including an older walking track, that once did not experience submersion during high tide and springtide events are now periodically inundated with estuarine water.

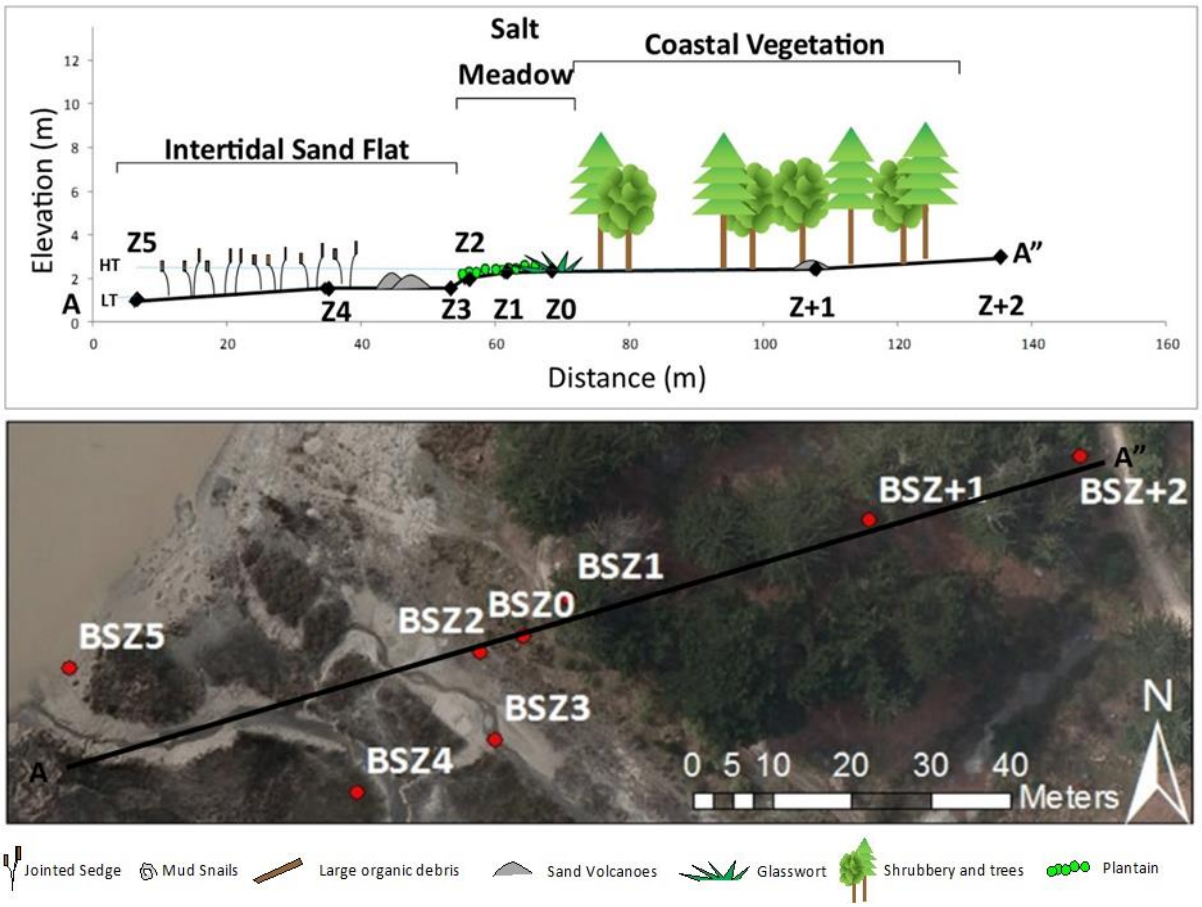


Figure 3.2: Idealised graphic transect (above) and corresponding satellite image (below) of the Bridge St transect, a key has been provided at base of figure 3.2.

The transect runs west-southwest with the highest sampling point being BSZ+2. BSZ+2 is found midway up the stop-bank which borders this area and as the highest point on this transect it is the only site which does not experience periodic inundation of estuarine water. The foliage of the area consists mainly of grass, with sporadic leaf and twig debris on top of soil and river bed material. Sample site BSZ+1 is on a grassed area with a reduced amount of macrocarpa, as it is one of three sample zones on the BS transect that prior to the February 2011 Earthquake was not affected by tidal inundation. This site lacks the abundance of grass, with more open areas, and higher levels of foliage debris. Additionally this location was at one point heavily influenced by liquefaction, with old semi preserved sand volcanoes still present. BSZ0 is the final site that has been influenced by tidal inundation, compared with sample zones higher on this transect a noticeable change in foliage occurs, changing from macrocarpa and leafy ground covered foliage to a plantain dominated area. BSZ1 coincides with a similar setting, dominated by plantain and the gradual introduction of glasswort, additionally as BSZ1 is closer to the river channels it experiences longer periods of inundation between high and low tide. BSZ2 coincides with a change in foliage type to predominantly glasswort, a low lying fleshy vegetation. BSZ3 is located inside an active channel, away from any form of vegetation. Although remnants of sand volcanoes are seen nearby this site was intentionally located within the channel away from sand volcano features. BSZ4 is located amongst the lower channels under dense jointed sedge bushes and is subject to long periods of inundation between tidal changes. Finally BSZ5 is the termination point of the Bridge Street transect, located on the edge of the Avon River and jointed sedge zone at the low tide and is only exposed at low tide

3.2.2 Settlers Crescent

The Settlers Crescent (SC) (Figure 3.3) transect site is located behind a row of commercial buildings near the mouth of the Heathcote River. At low tide this locality has large expanses of tidal mud flats, with patches of dense Juncus midway between high and low tide zones. At the upper limits tidal channels transition suddenly into glasswort beds and then a gradual increase in Plantain occurs. Semi-preserved sand volcanoes are present, but not abundant. The upper limit of this transect is SCZ1, situated among a large area of glasswort (Figure 3.3). SCZ2 is positioned in the middle of a tidal channel and purposefully separated from remnant sand volcano deposits. SCZ3 was collected from the middle of a small clump of Juncus, half way out into the tidal mudflat area. SCZ4 was collected at the midway point between the jointed sedge zone of SCZ3 and low tide at the edge of the Heathcote River. Ending the SC transect is SCZ5, at the edge of the Heathcote River where sheets of *Ulva* (sea lettuce) were present.

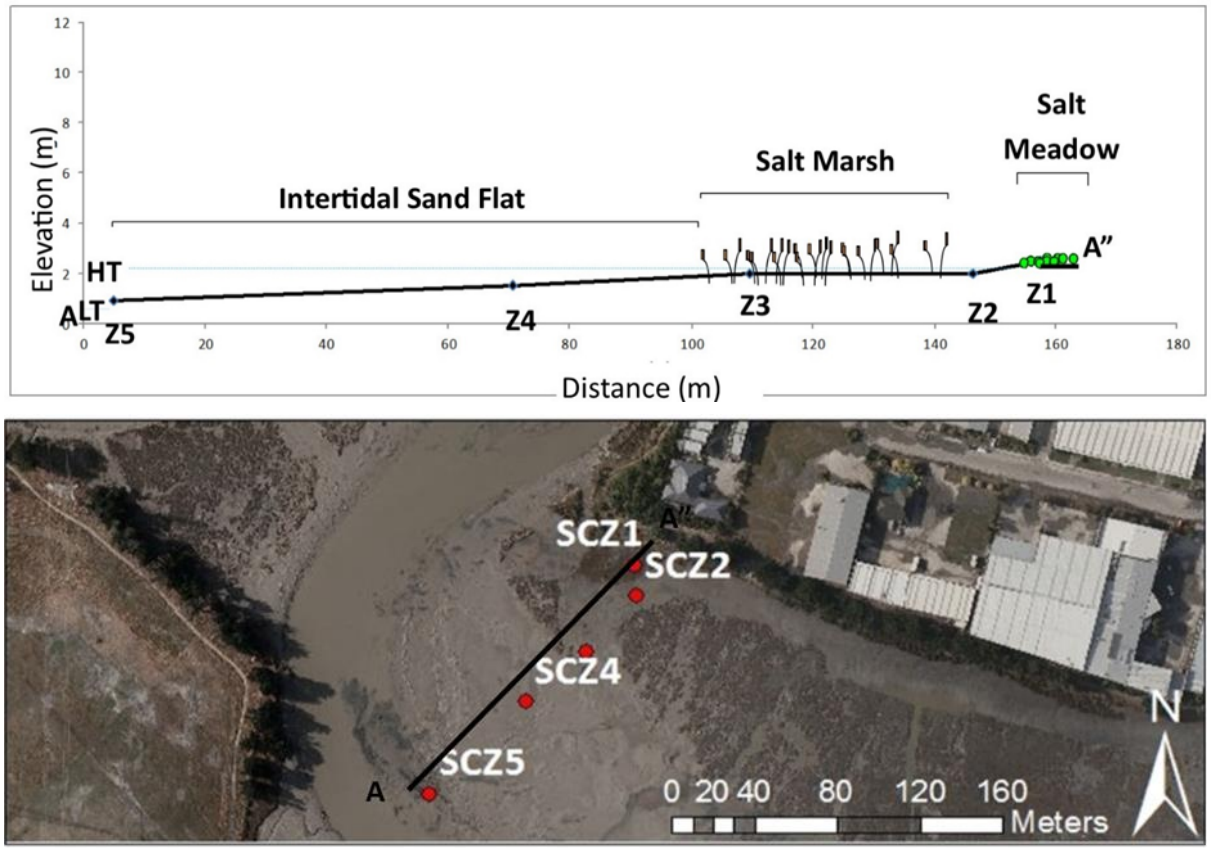


Figure 3.3: Idealised graphic transect (above) and corresponding satellite image (below) of the Settlers Cres. Refer to figure 3.2 for transect key.

3.2.3 McCormacks Bay

The McCormacks Bay (McB) (Figure 3.4) site borders the southern side of the AHE, bounded by Main Road and McCormacks Bay Road. McB is a relatively small tidally influenced reserve, draining from a single man-made inlet running below Main Road. The McCormacks Bay Reserve is host to recreational facilities such as rugby grounds and walking tracks. This locations transect is only 5m long, with a severe change in elevation from the built up rugby fields into the reserves tidal mudflat.

McBZ1 sits on the high tide mark, where samples are semi scraped off the raised embankment. Vegetation includes plantain, fleshy grasses and moss. McBZ2 drops onto the beach proper. Some shelly material is present with organic debris littering the surrounding surface. McBZ3 is sampled from the edge of the mud flat area, where high abundances of mud snails are littering the surface. Organic debris is found at lower concentrations but an increase in green algae is recorded. McBZ4 is the final sample site for this transect, found midway between the mud flat zone and the low tide water. This area hosts many mud snail shells, but in a much reduced amount than McBZ3. Further sample sites (Z5) were inaccessible due to the increasing mud component of the tidal flat making accessing this zone impossible.

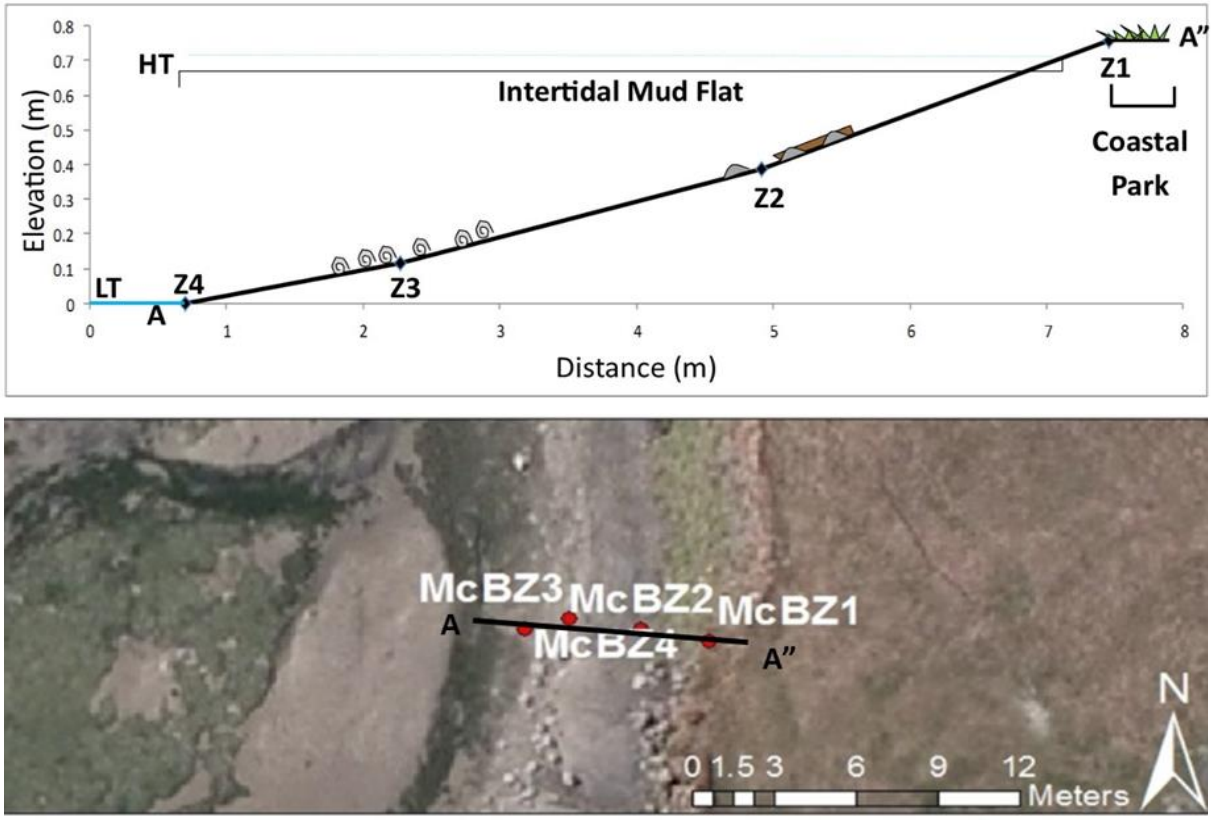


Figure 3.4: Idealised graphic transect (above) and corresponding satellite image (below) of the McCormacks Bay transect. Refer to figure 3.2 for transect key.

3.2.4 Southshore

South Shore (SS) (Figure 3.5) constitutes the eastern boundary of the AHE, although this is a rather large section of the Estuary samples for this study were only taken between Tern Street and Petrel Lane. Only three samples are recovered from this area, two from SSZ1, the first being sediment taken from below the Juncus plants, and the second being taken from below glasswort foliage. Both of these sites are at the edge of the sharp transition zone between sandy tidal mudflats and salt meadow. SSZ3 is taken a substantial distance out into the flat next to a ponded water body. Some *Ulva* was present but otherwise no indication of organic debris was seen.

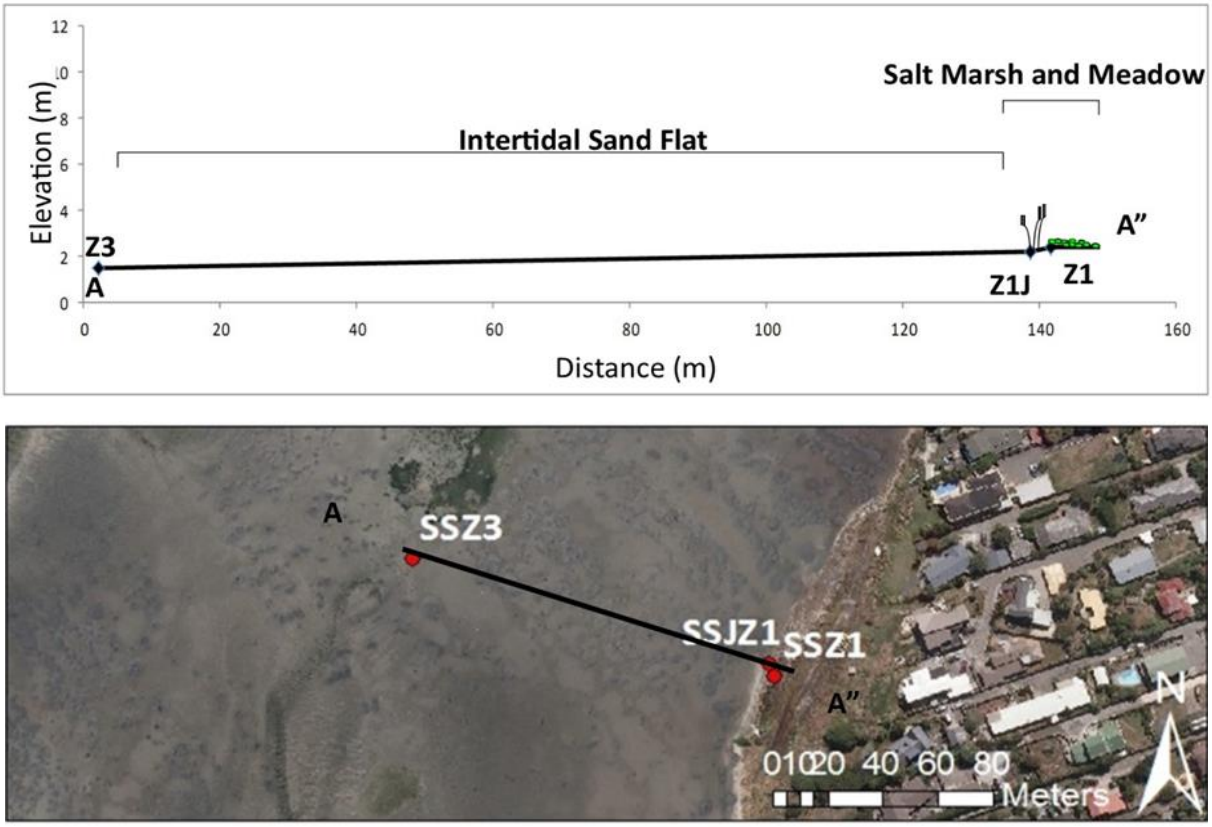


Figure 3.5: Idealised graphic transect (above) and corresponding satellite image (below) of the Southshore transect. Refer to figure 3.2 for transect key.

3.2.5 Moncks Bay

Moncks Bay (MB) site is located near the Estuary mouth, alongside Main Road, east of McCormacks Bay. This section of the estuary is channelized and provides mooring for private yachts, as well as a boat ramp and pier. Due to its location and proximity to the ocean-estuary interface this site is also influenced by minor wave action as well as regular and extensive recreational usage.

The upper section of the Moncks Bay, site MBZ1 is a man made embankment comprised of cobble–boulder sized clasts. Material which has been dislodged from the embankment surrounding Moncks Bay litter the upper regions of the beach, the same area from which sample MBZ1 was collected from. *Ulva* is present in moderate abundance, covering sections of sediment as well as the larger clasts. MBZ3 is a sandy area midway down the beach. Some rocks are present in the surrounding area as are green algae patches. MBZ5 is sampled at the lowest point of this transect, on the beach/water interface where small consistent wave action is occurring

3.3 RESULTS OF ENVIRONMENTAL FACTORS

3.3.1 Temperature, conductivity, salinity and pH

Salinity and conductivity measurements have a typically variable distribution around the AHE with high concentrations of 13.6-11.4 ppt recorded near the estuary mouth and lower concentrations 6.18(BS) and 3.5 ppt (SC) occurring at river inlets (Table 3.1). The pH readings are relatively homogenous across the estuary, aside from the Southshore site which records 8.72. Temperature does fluctuate between transect sites but this is expected with standing water bodies recording higher temperature than those that have a constant influx of fresh water.

Table 3.1: Characteristics of transect locations around the AHE. Temperature (°C), conductivity (mS), salinity (ppt) and pH.

	Temperature (°C)	Conductivity (mS)	Salinity (ppt)	pH
Bridge St				
River	16.2	12.25	6.18	7.65
Ponded	23.4	17.4	8.7	8.08
Settlers Cres				
River	14.7	7	3.5	7.31
Ponded	13.4	18.4	9.2	6.59
McCormacks Bay				
River	9.5	25.6	15.6	12.8
Moncks Bay				
River	15.2	23	11.4	7.95
Southshore				
Ponded	23.6	27.5	13.6	8.72

Salinity in the AHE ranged from 13.6ppt at Southshore to 8.7ppt at Bridge St in ponded (cut off still water bodies) samples and 15.6ppt at McCormacks Bay to 3.5ppt at Settlers Cres in river (flowing water or main estuary water body) samples. Ponded samples are expected to have higher salinity readings as they have been subject to evaporation. The highest salinities were recorded near the estuary – ocean interface with lowest salinities at the river. Conductivity follows the same trend as salinity, with higher conductivity at the estuary – ocean interface, and lower conductivity at the river mouths, river results vary from 25.6mS at McCormacks Bay to 7mS at Settlers Cres and ponded results are higher than there river counterparts. The pH readings are relatively homogenous across

the estuary, with river results ranging from 7.95 at Moncks Bay to 7.31 at Settlers Cres and ponded ranging from 8.72 at Southshore to 6.59 at Settlers Cres. Temperature recorded from river samples had a maximum of 16.2 ^{o}C at Bridge St and a minimum of 9.5^{o}C at McCormacks Bay while ponded samples were extremely variable with 23.6^{o}C at Southshore and 13.4^{o}C at Settlers Cres. All results from this section are presented in table 3.1.

3.3.2 Grain size distribution

The modern estuary exhibits a wide range of sediment textures which vary from almost entirely sand (93%) to over 80% silt and clay components, most of which though have a more dominant sand component (Figure 3.6). Settlers Cres, Bridge St and McCormacks Bay transects generally have a sediment distribution with course grained material (sand) being abundant at higher elevations, and fine grained material (silt and clay) becoming progressively more abundant with lower elevation. Southshore exhibits the reverse trend to McCormacks Bay, Settlers Cres and Bridge St with fine grained material becoming less abundant at lower elevations and Moncks Bay has no distinguishable trend, with variable results across its length. Over all the closer to the estuary ocean interface a transect site is the more fine grained material it will have. McCormacks Bay is an exception to this trend as it has significantly more silt and clay than all other transects. This difference is likely due to its enclosed nature, having extremely limited drainage and a low energy system where sediment eroded from the surrounding cliffs is not removed with any efficiency (Figure 3.6).

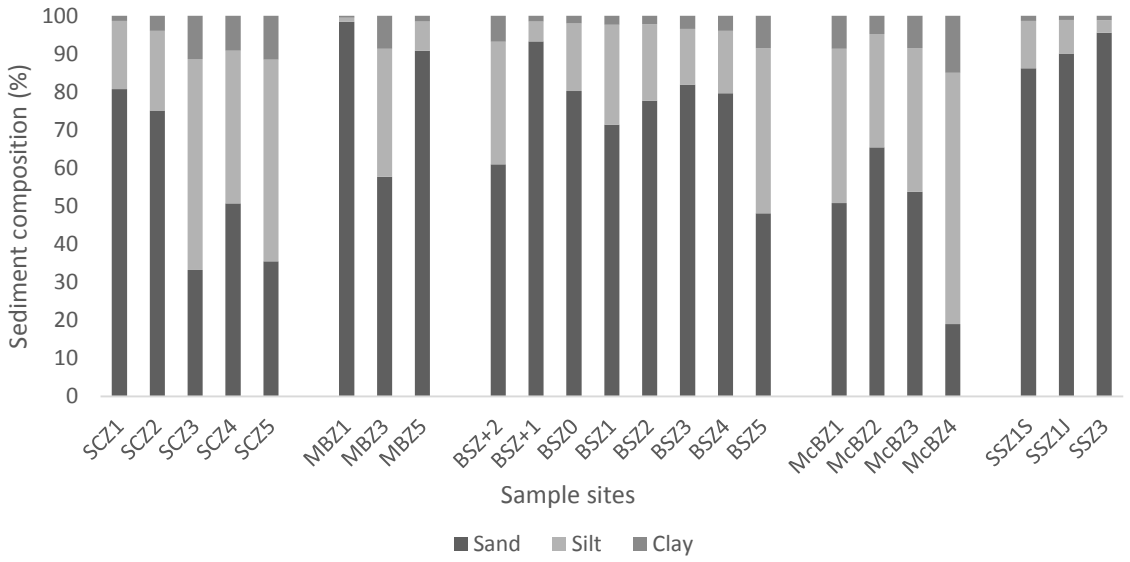


Figure 3.6: Proportional abundance of general grain size (clay, silt and sand) for individual sample zones at each transect location around the AHE.

3.3.3 Organic Carbon

The organic carbon content in the modern AHE ranged from 0.08% to 6.50% (Figure 3.7). The concentrations of organic carbon at BSZ0, BSZ1 and McBZ1 were higher than all other sites which may be due to all three sites been sampled in areas abundant in rootlets and living plants, thus having a soil component. No distinct pattern is identifiable between transects and within individual transects.

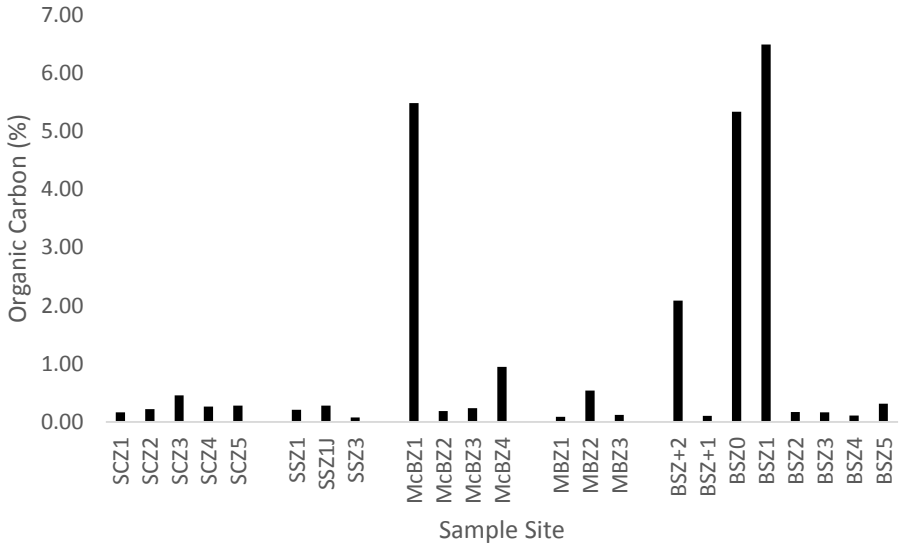


Figure 3.7: Percentage of organic content in sediments at Bridge Street (BS); Settlers Crescent (SC); McCormacks Bay (McB); Moncks Bay (MB) and Southshore (SS).

3.4 GEOCHEMISTRY

3.4.1 Bridge Street

Arsenic has a maximum concentration of 15 mg/kg^{-1} (Z0) a minimum of 2 mg/kg^{-1} (Z+1) and an average of 5.5mg/kg^{-1} over the entire transect. Most recorded values fall between 5.3 mg/kg^{-1} and the minimum value except for from one substantial spike in concentration at Z0 (14.6 mg/kg^{-1}).

Cadmium is homogenous along the BS transect with a maximum concentration of 0.13 mg/kg^{-1} (Z+2) and a minimum concentration of 0.01 mg/kg^{-1} (Z+1). Average concentration is 0.05 mg/kg^{-1}, and on a small scale fluctuations are seen from Z+2 – Z5. These fluctuations do not correlate with changes in elevation or grain size.

Chromium concentration fluctuates within the BS transect, with a maximum concentration of 26.7 mg/kg^{-1} (Z+2), minimum of 6.6 mg/kg^{-1} (Z+1) and averaging 13.4 mg/kg^{-1}. Z+2 records a

substantially higher Cr concentration with 26.7 mg/kg^{-1}, remembering that Z+2 stop bank material is sourced from outside the AHE, and does not reflect the immediate regions geochemistry.

Cobalt concentration stays relatively stable along the BS transect, with a maximum of 5.3 mg/kg^{-1} (Z+2), minimum of 3.1 mg/kg^{-1} (Z+1) and an average concentration of 4mg/kg^{-1}.

Copper concentration is highly variable throughout the BS transect with a maximum of 15.4 mg/kg^{-1} (Z1), minimum of 1.8 mg/kg^{-1} (Z+1) and an average 8 mg/kg^{-1}. Z1, 2, 4 and 5 are all extremely low in Cu, while the remaining sample sites are highly enriched.

Lead concentrations are moderately variable, with one extremely enriched sample (Z0 – 351.1 mg/kg^{-1}) and a minimum value of 4.9 mg/kg^{-1} (Z+1) and average of 66.5 mg/kg^{-1}.

Manganese concentrations in the BS sediment samples are extremely variable with a maximum concentration of 248.8 mg/kg^{-1} (Z0), a minimum of 125mg/kg^{-1} (Z+1) and an average of 192.8 mg/kg^{-1}.

Nickel concentrations are relatively stable, recording low level fluctuations between sample sites on the BS transect. Ni reaches a maximum concentration of 10.1 mg/kg^{-1} (Z1), a minimum of 4.9 mg/kg^{-1} (Z+1) and an average of 8 mg/kg^{-1}.

Zinc fluctuates throughout the BS transect, with a maximum concentration of 92.2 mg/kg^{-1} (Z+2), a minimum of 21.5 mg/kg^{-1} (Z+1) and an average of 55.5 mg/kg^{-1}.

Trace metal concentration relative to clay percentage for the Bridge St transect is variable in regards to results being positive or inverse but all of them are extremely weak, with very low R^2 values. Z+2 as stated earlier in chapter 2 is a large stop bank which has been constructed from material taken from the Avon River, and as such does not accurately reflect the geochemistry of the Bridge Street area. Z+1 may also be removed, as it too may not accurately reflect the local geochemistry by being liquefaction sediment.

3.4.2 Settlers Crescent

Arsenic has a maximum concentration of 5.9 mg/kg^{-1} (Z3) a minimum of 2.2 mg/kg^{-1} (Z3) and an average of 4 mg/kg^{-1} over the entire transect

Cadmium is homogenous along the SC transect with a maximum concentration of 0.11 mg/kg^{-1} (Z5) and a minimum concentration of 0.01 mg/kg^{-1} (Z1). Average concentration is 0.04 mg/kg^{-1}, and on a small scale fluctuations occur between Z1 – Z5.

Chromium concentration fluctuate weakly through the transect, with a maximum concentration of 18.9 mg/kg^{-1} (Z3), minimum of 10.8 mg/kg^{-1} (Z1) and averaging 15.1 mg/kg^{-1}.

Cobalt concentration is stable along the SC transect, with a maximum of 5 mg/kg^{-1}(Z2), minimum of 3.1 mg/kg^{-1} (Z1) and an average concentration of 4.4 mg/kg^{-1}.

Copper concentration is slightly variable with a maximum of 11.2 mg/kg^{-1} (Z5), minimum of 4.9 mg/kg^{-1} (Z1) and an average 7.6 mg/kg^{-1}.

Lead concentrations are moderately variable with a maximum of 24.2 mg/kg^{-1} (Z3), a minimum of 4.9 mg/kg^{-1} (Z1) and an average concentration of 15.3 mg/kg^{-1}.

Manganese concentrations in the SC sediment samples fluctuate moderately with a maximum concentration of 245.9 mg/kg^{-1} (Z2), a minimum of 202.4 mg/kg^{-1} (Z1) and an average of 219.6 mg/kg^{-1}.

Nickel concentrations are stable along the SC transect, Ni reaches a maximum concentration of 10 .2 mg/kg^{-1}, a minimum of 8.5 mg/kg^{-1} and an average of 9.5 mg/kg^{-1}.

Zinc generally increases in concentration from Z1 to Z5 along the SC transect, with a maximum concentration of 100 mg/kg^{-1} (Z4), a minimum of 28 mg/kg^{-1} (Z1) and an average of 60.6 mg/kg^{-1}.

Aside from Manganese all trace metals exhibit a positive trend with increasing clay proportions at Settlers Cres. Cr, Cu, Ni and Zn have high R^2 values while As, Cd, Co and Pb have moderate to low R^2 values and manganese being the sole trace metal in Settlers Crescent recording an inverse relationship with clay percentage, which is extremely weak.

3.4.3 McCormacks Bay

Arsenic has a maximum concentration of 4.9 mg/kg^{-1} (Z4) a minimum of 2.2 mg/kg^{-1} (Z2) and an average of 4 mg/kg^{-1} over the entire transect.

Cadmium records small scale fluctuations along the McB transect with a maximum concentration of 0.17 mg/kg^{-1} (Z4), a minimum concentration of 0.02 mg/kg^{-1} (Z2) and an average concentration is 0.07 mg/kg^{-1}.

Chromium concentrations along the transect record a maximum of 21.8 mg/kg^{-1}(Z4), a minimum of 3.8 mg/kg^{-1} (Z2) and averaging 12.8 mg/kg^{-1}.

Cobalt concentration stays relatively stable along the McB transect with only minor fluctuations, with a maximum of 9.0 mg/kg^{-1} (Z1), minimum of 3.8 mg/kg^{-1} (Z3) and an average concentration of 5.8 mg/kg^{-1}.

Copper concentration is highly variable throughout the McB transect with a maximum of 14.7 mg/kg^{-1} (Z4), minimum of 4.4 mg/kg^{-1} (Z2) and an average 9.4 mg/kg^{-1}.

Lead concentration records a maximum of 22.1 mg/kg^{-1} (Z4), a minimum of 7.4 mg/kg^{-1} (Z2) and an average concentration of 14.2 mg/kg^{-1}.

Manganese concentrations in the McB sediment samples are extremely variable with a maximum concentration of 394.4 mg/kg^{-1} (Z1), a minimum of 152.3 mg/kg^{-1} (Z2) and an average of 238.2 mg/kg^{-1}.

Nickel concentrations only record minor fluctuations, with a maximum concentration of 13.1 mg/kg^{-1} (Z4), a minimum of 6.5 mg/kg^{-1} (Z2) and an average of 10.1 mg/kg^{-1}.

Zinc concentrations throughout the McB transect are quite variable, with a maximum concentration of 99.8 mg/kg^{-1} (Z4), a minimum of 29.8 mg/kg^{-1} (Z1) and an average of 62.8 mg/kg^{-1}.

All trace metal samples in the McCormacks Bay transect exhibit a positive relationship with increasing clay levels, most of which (As, Cd, Cr, Cu, Pb, Ni, Zn) have high R^2 values. A further trend which is recorded in all trace metals, aside from cadmium, is a double spike in concentrations, one at Z1 and the second at Z4 (upper and lower extent of the transect). Both Z1 and Z4 have comparatively high clay proportions in comparison to other sample sites on this transect, which is the likely reason for them to record high trace metal concentrations.

3.4.4 Moncks Bay

Arsenic has a maximum concentration of 4.1 mg/kg^{-1} (Z5), a minimum of 2 mg/kg^{-1} (Z1) and an average of 3 mg/kg^{-1}.

Cadmium records small scale fluctuations along the MB transect with a maximum 0.05 mg/kg^{-1} (Z5), a minimum of 0.01 mg/kg^{-1} (Z1) and an average of 0.03 mg/kg^{-1}.

Chromium concentrations along the transect record a maximum of 15 mg/kg^{-1} (Z5), a minimum of 8.1 mg/kg^{-1} (Z1) and an average of 11.2 mg/kg^{-1}..

Cobalt concentration stays relatively stable along the MB transect with only minor fluctuations, with a maximum of 5.5 mg/kg^{-1} (Z5), a minimum of 3.4 mg/kg^{-1} (Z1).

Copper concentration is highly variable throughout the MB transect with a maximum of 6.6 mg/kg^{-1} (Z5), a minimum of 1.9 mg/kg^{-1} (Z1) and an average of 3.9 mg/kg^{-1}.

Lead concentration records a maximum of 13.1 mg/kg^{-1} (Z5), a minimum of 6 mg/kg^{-1} (Z1) and an average of 8.9 mg/kg^{-1}.

Manganese concentrations in the MB sediment samples record a maximum concentration of 290.4 mg/kg^{-1} (Z5), a minimum of 162.7 mg/kg^{-1} (Z1) and an average of 216 mg/kg^{-1}.

Nickel concentrations only record minor fluctuations, with a maximum concentration of 11.4 mg/kg^{-1} (Z5), a minimum of 6.6 mg/kg^{-1} (Z1) and an average of 8.9mg/kg^{-1}.

Zinc concentrations throughout the MB transect are quite variable, with a maximum concentration of 50.1 mg/kg^{-1} (Z5), a minimum of 27.8 mg/kg^{-1} (Z1) and an average of 37.7 mg/kg^{-1}.

The Moncks Bay transect shows a consistent trend across all measured trace metals, with the lowest concentrations recorded at Z1 (highest elevation) and the highest concentration recorded at Z5 (lowest elevation). Interestingly this trend does not coincide with clay percentage distribution along the transect. The relationship between trace metal concentration and the percentage of clay within each sample site, for the most part, exhibit an inverse relationship, with only As, Co and Ni recording positive relationships. Unfortunately all the R^2 values for trace metal and clay are extremely low, with the highest R^2 value being 0.05 (Cd) and the lowest being 0.008 (Ni).

3.4.5 Southshore

Southshore geochemistry is based off two sample sites, unfortunately, because of this, inference to relationships with relative grain size or site elevation cannot be produced. As only a single site has been sampled for trace metals, results have been presented in a table format (Table 3.2).

Table 3.2: Southshore trace metal concentration data in mg/kg^{-1}.

	As	Cd	Cr	Co	Cu	Pb	Mn	Ni	Zn
Z1	3.1	0.0	8.7	3.5	2.4	6.9	168.8	7.4	31.5

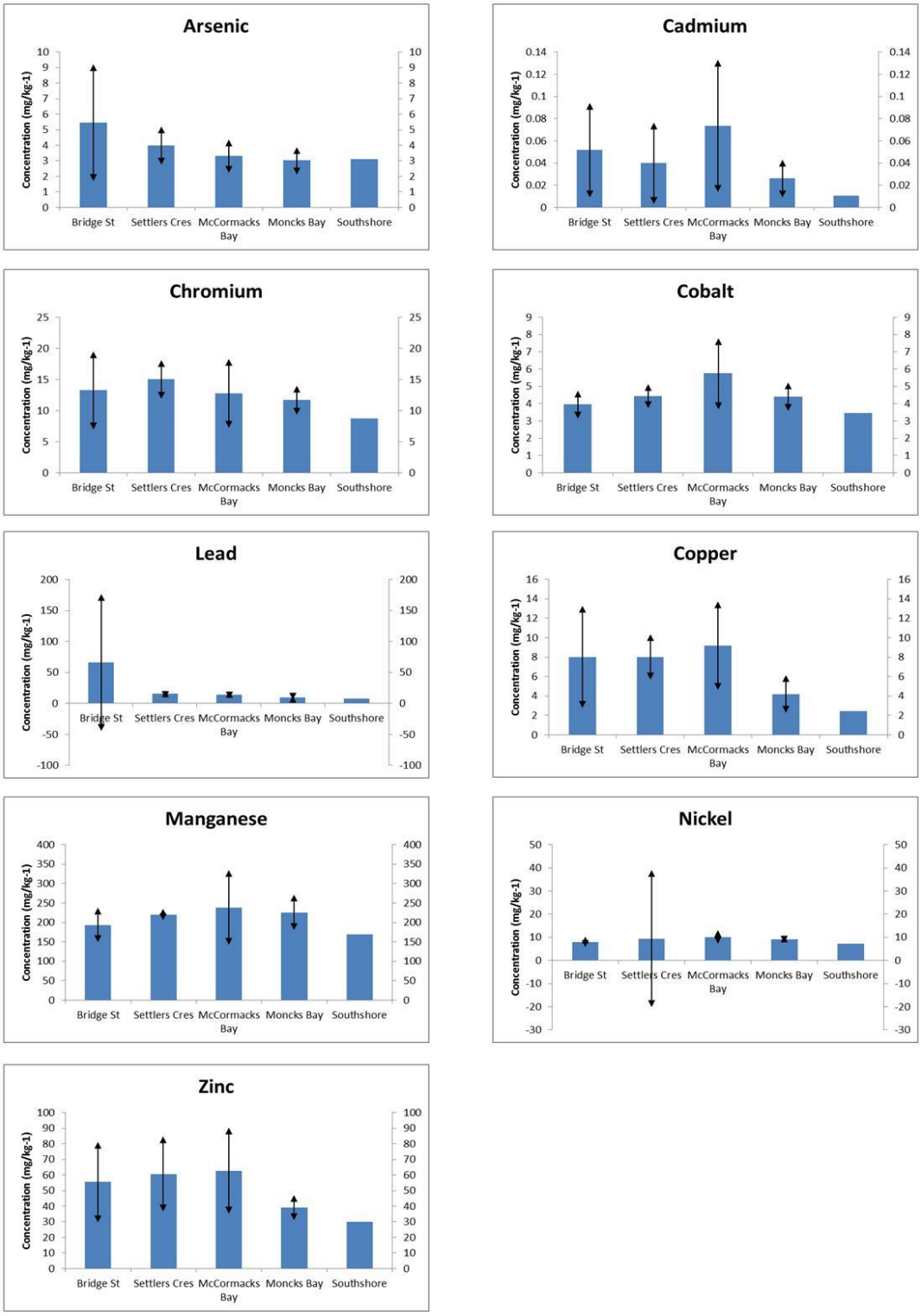


Figure 3.8: Average trace metal concentration with highest and lowest extremes.

3.4.5 Trace metal concentrations around the AHE

When trace metal results for each location are viewed as transect averages (Figure 3.8) it becomes apparent that trace metal concentrations are relatively homogenous between transect locations. However a few exceptions do stand out, these being a large spike in Pb concentrations at the Bridge St transect and variable concentrations for Zn in Bridge St, Settlers Cres and McCormacks Bay transects. A potential explanation for the Bridge St Pb spike is that at the time of sampling, high levels of road works were occurring in nearby areas. Because of these road works heavy machinery was being used extensively and this spike could be result of this. Additionally a potential source of lead based paint from the nearby Bridge St bridge may also be an influence. High Zn concentrations at BS, SC and McB may potentially be the result of their locations. All transect locations are close to sources of rain and storm outflow water (Avon River for BS, Heathcote River for SC and the enclosing Port Hill spurs where residential properties are abundant).

Australia and New Zealand adhere to guidelines set up in order to quantify acceptable levels of contamination in sediment (ANZECC) (Table 3.3). If trace metal concentrations fall below the ANZECC ISQG-Low levels the trace metal is unlikely to cause any biological impact on organisms inhabiting that sediment. If trace metal concentrations exceed the ANZECC ISQG-High level it is highly likely that any organism inhabiting that sediment will be effected in some way.

Table 3.3: ANZECC ISQG-Low/High guidelines to quantify "acceptable" levels of contamination in sediment.

Contaminant	ISQG-Low (mg/kg^{-1})	ISQG-High (mg/kg^{-1})
Arsenic	20	70
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Nickel	21	52
Zinc	200	410

Figure 3.9 also shows the average concentrations of trace metals across the AHE relative to New Zealand ISQG-Low contamination standards. All of the trace metal concentrations were less than ANZECC ISQG-low guidelines aside from lead at Bridge St.

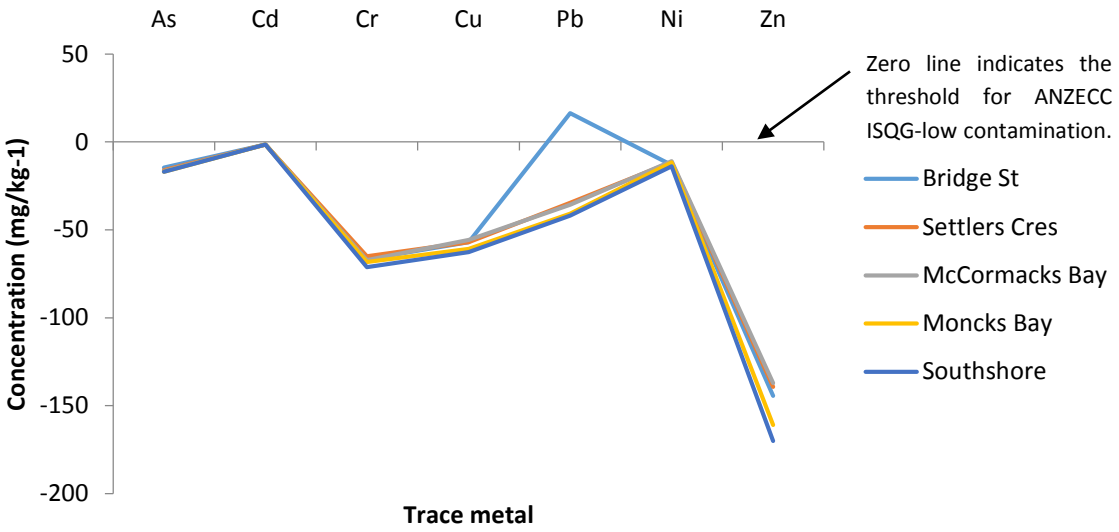


Figure 3.9: Spider diagram of trace metal averages throughout the modern AHE. Figure 3.8 also exhibits trace metals relative to ANZECC ISQG-low pollution guidelines (Zero) trace metals which go above the zero line have a higher concentrations than what is accepted for soil contamination levels.

3.5 POLLUTION INDEXES

Pollution indexes results indicate that pollution is generally similar in concentrations across the AHE. Four sample sites are outliers with elevated pollution levels, these being BSZ+2, BSZ0, BSZ1 and McBZ4 (Table 3.4). When regarding individual trace metal concentrations for each site BSZ+2 has elevated levels of Cr and Pb, BSZ0 has extremely elevated levels of Pb (only site with a trace metal which is over the NZ ISQG low levels), BSZ1 which has high concentrations of Cr, Pb and Ni and McBZ1 with has elevated concentrations of Pb, Zn and Cr.

Table 3.4: Results of pollution indexes PLI, MPI and mCd

	PLI	MPI	mCd
BSZ+2	13.907	1.040972	1.295074
BSZ+1	1.007141	0.279733	0.341333
BSZ0	910.1844	1.285948	3.26764
BSZ1	9.18343	1.002033	1.41605
BSZ2	1.030626	0.385605	0.463854
BSZ3	2.135379	0.789532	0.903866
BSZ4	1.039628	0.407935	0.480433
BSZ5	1.073586	0.4664	0.557516
SCZ1	1.024229	0.366299	0.447248
SCZ2	1.1819	0.564118	0.672216
SCZ3	1.779015	0.742674	0.867249
SCZ4	1.430277	0.668121	0.755933
SCZ5	3.367482	0.876509	1.052259
McBZ1	3.669242	0.889913	1.001816
McBZ2	1.032623	0.390973	0.442695
McBZ3	1.104479	0.502573	0.584592
McBZ4	20.14796	1.071901	1.333548
MBZ1	1.013436	0.321697	0.400337
MBZ3	1.057941	0.443001	0.528942
MBZ5	1.582091	0.706028	0.813273

3.6 RELATIONSHIPS BETWEEN ENVIRONMENTAL FACTORS

Spearman's correlation identified that multiple correlations exist between environmental factors. Pollution indexes and organic carbon have a significant correlation within sampled sediments, showing a positive correlations with PLI ($P<0.001$), MPI ($P<0.001$) and mCd ($P<0.001$) while sand has a negative correlation with PLI and MPI ($P<0.05$) and silt has the same relationship but with a positive correlation (Table 3.5). Correlations were identified between sediment composition and organic carbon ranging from $P<0.01$ with silt and sand to $P<0.05$ with clay. Elevation did not correlate with any other environmental factor.

Table 3.5: Spearman's correlation comparing pollution indexes, grain size components, individual trace metals and organic content, * = highly significant (0.001), ** = very significant (0.01), * = just significant (0.05).**

	PLI	MPI	mCd	Sand	Silt	Clay	Carbon	Elevation
PLI	1.00							
MPI	1.00***	1.00						
mCd	0.99***	0.99***	1.00					
Sand	-0.45*	-0.45*	-0.42	1.00				
Silt	0.45*	0.45*	0.42	-0.99***	1.00			
Clay	0.44	0.44	0.39	-0.94***	0.92***	1.00		
Carbon	0.78***	0.78***	0.77***	-0.66**	0.68**	0.56*	1.00	
Elevation	-0.08	-0.08	-0.07	0.32	-0.28	-0.43	0.04	1.00

3.7 LIVE VERSE DEAD DIATOMS

Comparison of live diatom samples (LDS) with dead diatom samples (DDS) used in chapter three was undertaken using a simple two tailed t-Test assuming unequal variance. Each sample taken from the Bridge St transect was compared individually against the LDS with the exception of BSZ+1 in which no diatom valves were observed (liquefaction sediment) (Table 3.6).

Results with P-values equal to or over the assigned alpha value (0.05) indicate an agreement with the null hypothesis, meaning that the two data sets are similar. In this case all P-values analysed are greater than 0.05 indicating that BSZ+1, BSZ0, BSZ1, BSZ2, BSZ3, BSZ4 and BSZ5 are similar to the live diatom sample (Table 3.6). This comes as a relief as it validates that surface samples can be used as an representation of what is living in the estuary, and thus how the estuary has been influenced by changes in the environment and additionally have since recovered from the abrupt change in elevation, now being stable.

Table 3.6: Results of t-Test two sample assuming unequal variance for live vs dead diatom samples.

	BSZ+2	BSZ0	BSZ1	BSZ2	BSZ3	BSZ4	BSZ5	LDS
Mean	2.120567	2.163121	2.248227	2.056738	2.007092	1.893617	2.099291	2.078014
Variance	53.30679	52.73749	74.17366	48.1539	65.83566	60.66717	55.61864	64.00101
Observations	141	141	141	141	141	141	141	141
df	278	277	278	275	280	280	279	
P(T<=t) two-tail	0.962823	0.925548	0.863607	0.980985	0.941136	0.844671	0.981587	
t Critical two-tail	1.968534	1.968565	1.968534	1.968628	1.968472	1.968472	1.968503	

3.8 MODERN DIATOM ASSEMBLAGES

Details of diatoms from each sample site are given in appendix (A), and the species data are summarised below.

3.8.1 Location assemblages

A total of 142 species in 40 genera are identified across the modern samples, species identified is much higher than McClatchie, (1982) but overall abundance of valves in slides was much lower. General diatom assemblages (BS, SC, SS, and McB) are characterised below by the most abundant species. Overall species abundance is high and preservation is relatively good, although areas with coarse grain sizes generally have a lower level of preservation. Moncks Bay does not have a general assemblage, nor is it included in any species or site associations as no valves were identified from any of the three sampled sites.

Bridge St:

Dominant species: *Achnanthes clevei*

Secondary species: *Amphora coffeaeformus, Cocconeis placentula, Gomphonema* sp1*, Hantzschia amphoxys, Melosire nummuloides, Navicula cryptotenella, Nitzschia amphibia, Psammothidium subatomoides.*

Summary: Bridge Street, on the northern side of the AHE, has a high abundance of diatom valves that are moderately to well preserved. Diversity indices for this location are high and furthermore species indicate a dominantly fresh water preference for this location, but does have a minor brackish component.

Settlers Crescent:

Dominant species: *Navicula perminuta*

Secondary species: *Achnanthes clevei, Amphora coffeaeformus, Cocconeis placentula, Nitzschia amphibia, Opephora guenter-grassii, Pseudostaurosira* sp1*, Planothidium linkei, Gomphonema* sp1*, Amphora* sp2*.*

Summary: Species diversity is high and values are also well preserved. An even split between fresh and brackish to marine preferring species is observed at this location. Four of the representative species have not been linked to a salinity preference.

Southshore:

Dominant species: *Diploneis smithii*

Secondary species: *Cocconeis placentula, Cocconeis scutellum var scutellum, Nitzschia amphibia,*

Navicula cincta, Grammatophora hamulifera, Eunotogramma marinum, Diploneis didyma, Fallacia sp1.

Summary: The South Shore assemblage has extremely low abundances and a very poor level of preservation. The species in this location indicate a split between freshwater and brackish marine environments. Some species that represent this site have not yet been associated with a salinity preference.

McCormacks Bay:

Dominant species: *Opephora guenter-grassii*

Secondary species: *Amphora coffeaeformus, Cocconeis placentula, Cocconeis scutellum var scutellum, Cocconeis scutellum var parva, Nitzschia amphibia, Navicula perminuta, Navicula vilaplanii, Navicula inconspicua, Navicula* sp4*.*

Summary: The McCormacks Bay assemblage is abundant in species, preservation is also moderate with a combination of preserved valves and broken fragments. This site is dominated by brackish to brackish marine species, with a small percentage preferring fresh water environments.

3.8.2 Modern species assemblages

PAST statistical software was used to determine similarities and differences between sample sites as well as relevant taxa, additionally cluster analysis were undertaken using past software to determine assemblages and the what environmental factors influenced the grouping of sites and assemblages. Bray-Curtis cluster analysis of modern diatom data produced 8 separate site clusters, and 10 distinct diatom associations (Figure 3.10) which are as follows. Known salinity preferences for each species is provided (F-fresh, FB-fresh brackish, FI-fresh indifferent, B-brackish, BM-brackish marine, BI-brackish indifferent and M-marine).

Species Assemblage 1 (Figure 3.10)

Species: *Navicula perminuta* (B) and *Opephora guenter-grassii* (BM).

Dominant sample association: B

Secondary sample associations: C, D, E, F

Summary: This association tends to concentrate in areas of muddy sands to sandy muds, No preference is apparent for pH levels or trace metal concentrations. Concentrations also occur in middle zones of both the SC and McB sample and most abundant in low tidal zones of McB and SC.

Species Assemblage 2 (Figure 3.10)

Species: *Navicula vilaplanii, Diploneis smithii* (B) *Navicula cinca* (F), *Navicula* sp4 *and Rhophalodia* sp1.

Dominant sample association: A

Secondary sample associations: B, D, E, F

Summary: Most abundant in SS, and in zones of moderate to high sand concentrations with high pH levels.

Species Assemblage 3 (Figure 3.10)

Species: *Navicula* sp12*, Nitzschia palae* (F)*, Cocconeis hauniensis* (BM)*, Nitzschia minuta, Achnanthes brevipes var intermedia* (BM) and *Navicula* sp2*.*

Dominant sample association: F

Secondary sample associations: C, D, E, G

Summary: This association is found almost exclusively in BS sites at mid-level tidal height zones with vegetation.

Species Assemblage 4 (Figure 3.10)

Species: *Navicula* sp10*, Navicula capitata var lunebergensis* (F)*, Navicula cryptocephala* (F)*, Navicula recens* (FB)*, Nitzschia capitellata* (B) and *Navicula cryptotenella* (F).

Dominant sample association: F

Secondary site associations: C, D, E, F, G

Summary: This association is most common in mid tidal range zones at Bridge St sample sites.

Species Assemblage 5 (Figure 3.10)

Species: *Fragilaria brevistriata* (FI)*, Geisselaris paludosa, Staurosirella pinnata, Melosire nummuloide* (B)*, Fragilaria* sp1*, Cocconeis speciosa* (BM) and *Hantzschia amphioxys* (FB)*.*

Dominant sample association: E

Secondary sample associations: C, D, F

Summary: This association is extremely common in zones above the tidal range (BSZ+2). Additionally this sample site is composed of introduced stop-bank material.

Species Assemblage 6 (Figure 3.10)

Species: *Amphora* sp3*, Nitzschia granulata* (BM)*, Nitzschia* sp5*, Navicula* sp17 *and Diploneis pneumatica* (M)*.*

Dominant sample association: E

Secondary sample associations: F, G

Summary: Species in this association are most common in low tidal height zones on the BS transect.

Species Assemblage 7 (Figure 3.10)

Species: *Achnanthes brevipes* (BM)*, Nitzschia clausii, Psammothidium subatomoides* and *Cocconeis scutellum var scutellum* (BM)*.*

Dominant sample association: G

Secondary sample associations: C, D, F

Summary: Species in this association are most common in high tidal zones of McB.

Species Assemblage 8 (Figure 3.10)

Species: *Achnanthes clevei* (F)*, Amphora* sp2*, Gomphonema* sp1*, Cocconeis scutellum var parva* (BI)*, Cocconeis placentula* (F)*, Nitzschia amphibia* (F) and *Achnanthes coffeaeformus* (BI)*, Achnanthes oblongella* (F).

Dominant sample association: C and D

Secondary sample associations: A, B, E, F, G

Summary: This association is most common in low tidal zones with no clear preference for site location.

Species Assemblage 9 (Figure 3.10)

Species: *Nitzschia inconspicua* (FB)*, Navicula geronimonsi* and *Opephora olsenii* (BM).

Dominant sample association: C

Secondary sample associations: B, F

Summary: This association is most commonly found in mid tidal range zones of SC and McB.

Species Assemblage 10 (Figure 3.10)

Species: *Navicula* sp3*, Planothidium* sp1*, Gomphonema* sp2*, Planothidium linkei, Pseudostaurosira* sp1*, Achnanthes* sp2*, Navicula* sp11*, Nitzschia compressa* (BM)*,* and *Nitzschia hungarica* (FB).

Dominant sample association: C

Secondary sample associations: B, D, E, F

Summary: This association is most commonly found in low tide zones of SC and infrequently in mid – high tide zones of McB and SC.

3.8.3 Modern site assemblages

Samples Assemblage A: (Figure 3.10)

Sample: SSZ1

Dominant species association: 2

Secondary species association: 7, 8

Sediment: sand

Diversity indices: H= 1.091, E=0.5955

Summary: This association is comprised of one sample site, in a sand dominated area where trace metal concentrations are low. Diatom preservation is low to moderate as is species diversity. This association is dominated by *Diploneis smithii* (52% abundance) and sub-dominated by *Navicula cincta* (35% abundance).

Samples Assemblage B: (Figure 3.10)

Sample: McBZ2, SCZ2

Dominant species association: 1, 2

Secondary species association: 8, 9, 10

Sediment: silty sand

Diversity indices: H=0.7248-1.969, E=0.2294-0.597

Summary: This association is comprised of two sample sites, both having grain sizes of silty sands. Trace metal concentrations, when compared with other sites are low, diatom preservation and diversity are high. This association is dominated by *Nitzschia compressa* (57% average abundance) and sub-dominated by *Amphora coffeaeformus* (8% average abundance).

Samples Assemblage C: (Figure 3.10)

Sample: McBZ3, McBZ4, SCZ3, SCZ4, SCZ5

Dominant species association: 1

Secondary species association: 3, 4, 5, 7, 8, 9, 10

Sediment: very silty sand – sandy silt

Diversity indices: H=1.32-2.534, E=0.3118-0.7415

Summary: This association is comprised of five sample sites, all of which are sandy silts. Trace metals between sites in this association are highly variable, diatom preservation is high as is species diversity. This association is dominated by *Opephora guenter-grassii* (34% average abundance) and is sub-dominated by *Amphora coffeaeformus* (9% average abundance).

Samples Assemblage D: (Figure 3.10)

Sample: BSZ3, BSZ4, BSZ5

Dominant species association: 6, 7, 8

Secondary species association: 1, 2, 3, 4, 5, 10

Sediment: very silty sand- silty sand

Diversity indices: H=2.257-2.494, E=0.5618-0.6201

Summary: This association is comprised of three sample sites, which range from silty sands to sands. Trace metal concentration in these sites are variable, diatom preservation is moderate and diatom diversity is high. This association is dominated by *Achnanthes clevei* (25.3% average abundance) and sub-dominated by *Psammothidium subatomoides* (9.7% average abundance).

Samples Assemblage E: (Figure 3.10)
Sample: BSZ+2
Dominant species association: 5
Secondary species association: 1, 2, 4, 8, 10
Sediment: silty sand
Diversity indices: H=2.353, E=0.7014

Summary: This association is comprised of one sample site, in a silty sand dominated area where trace metal concentrations are variable. Diatom preservation is low to moderate as is species diversity. This assemblage is dominated by *Cocconeis placentula* (20% abundance) and sub-dominated by *Opephora guenter-grassii* (14% abundance).

Samples Assemblage F: (Figure 3.10)
Sample: BSZ0, BSZ1, BSZ2
Dominant species association: 3, 4
Secondary species association: 1, 8, 10
Sediment: sand – silty sand
Diversity indices: H=2.382-2.509, E=0.6057-0.7217

Summary: This assemblage is comprised of three sample sites, in a sand dominated area. Diatom preservation and diversity for these sites are low to medium and trace metal concentrations are extremely variable. The dominant species for this assemblage is *Navicula cryptotenella* (14.3% average abundance) and sub-dominated by *Hantzschia amphioxys* and *Navicula capitata var lurebergensis* (8.3% average abundance).

Samples Assemblage G: (Figure 3.10)
Sample: McBZ1
Dominant species association: 7
Secondary species association: 3, 4, 6, 8
Sediment: very silty sand
Diversity indices: H=1.745, E=0.5727

Summary: This association is comprised of a single sample site, with a very silty sand grain size. Trace metal concentrations are variable between elements, diatom preservation is moderate and species diversity is low to moderate. This association is dominated by *Nitzschia amphibia* (41% abundance) and sub-dominated by *Psammothidium subatomoides* (14% abundance).

3.8.4 Modern species and site assemblage's summary

On observing the data presented in the modern assemblage cluster (Figure 3.10) a clear distinction between sites influenced by either the Heathcote (Red) or Avon (Blue) Rivers can be seen. Site associations B and C are made up of sites within or close to the Heathcote River mouth, while site associations D, E, and F are composed completely of Bridge St sampling sites which are influenced by the Avon River. Further distinction can be determined as sites B are composed of sampling sites which are lower on each transect while group C is composed of those found at higher elevations. Additionally for groups dominated by the Avon River a distinction is noticeable between D which is representative of sites found at the bottom of the Bridge St transect, sample association F which represents sites at the upper end and site association E representing the highest elevation of the Bridge St transect. This may indicate that these site association and the diatoms which compose them may be dominantly influenced by elevation and associated effects such as period of inundation while other environmental factors such as organics, trace metals or grain size are only secondary influences. Species association eight can be defined as a general AHE association as it is present in all site associations, and does not seem to be overly influenced by proximity to either the Avon or the Heathcote Rivers. Further confirmation that river proximity and elevation are the dominant influences on diatom assemblage comes from elimination of other environmental factors through the use of Spearman's correlation coefficient.

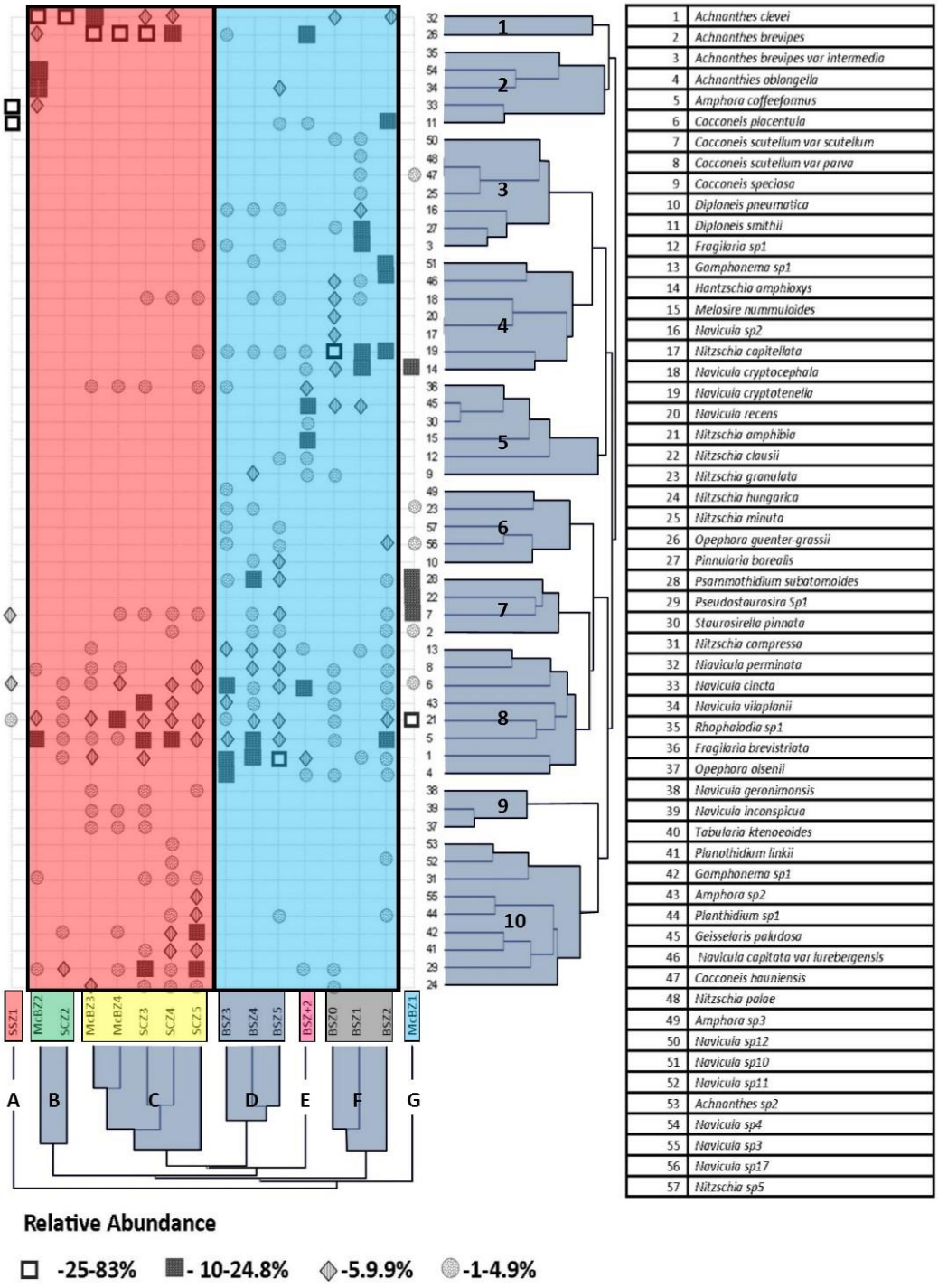


Figure 3.10: Modern diatom associations in the AHE, New Zealand. Ten distinct species associations and 7 distinct site associations developed when Bray-Curtis distance matrix is used to produce dendrogram classifications. Red and blue boxes indicate Heathcote (red) or Avon Rivers (blue) influence.

3.9 KEY SPECIES AND ENVIRONMENTAL FACTOR CORRELATIONS

To assist in determining how diatoms respond to changes in the environment and to help compare changes in diatom communities in both the modern and the core species with the highest abundance, and who were the most common through both the modern AHE and in the AHE core were selected as "Key Species". Diatoms which filled these criteria are *Achnanthes clevei, Cocconeis placentula, Cocconeis scutellum var parva, Navicula perminuta* and *Nitzschia amphibia*.

Spearman's ranked correlation indicated that of the five key species two exhibited a statistical relationship with environmental factors. Correlations between *Cocconeis scutellum var parva* and elevation were significant (P<0.001) and *Nitzschia amphibia* correlated with sand (P<0.05), silt (P<0.05) and clay (P<0.01) (Table 3.7).

Table 3.7: Spearman's ranked correlation of modern key diatom species and environmental factors. * = highly significant (0.001), ** = very significant (0.01), * = just significant (0.05)**.

	Achnanthes clevei	*Cocconeis placentula*	*Cocconeis scutellum var parva*	*Navicula perminuta*	*Nitzschia amphibia*
PLI	-0.29	0.24	-0.20	-0.46	-0.17
MPI	-0.29	0.24	-0.20	-0.46	-0.17
mCd	-0.26	0.23	-0.19	-0.47	-0.22
Sand	0.21	-0.11	-0.13	0.15	-0.58*
Silt	-0.24	0.08	0.10	-0.17	0.57*
Clay	-0.18	0.22	0.17	-0.17	0.68**
Carbon	-0.29	-0.09	-0.22	-0.34	-0.08
Elevation	-0.13	-0.34	-0.66**	0.30	-0.51

3.10 ENVIRONMENTAL FACTOR AND DIATOM VARIATION AROUND THE AHE

3.10.1 Kruskal-Wallis analysis

Significant variation in the concentration of clay was recorded across the AHE (P<0.05) while all other targeted environmental variables indicated negligible change in concentration (Table 3.8), critical values outlined in table 2.1.

Table 3.8: Kruskal-wallis analysis of variance on environmental factors.

	H	df	p
PLI	0.0196	2	0.9902
MPI	0.0196	2	0.9902
mCd	0.1768	2	0.9154
Sand	5.3821	2	0.06781
Silt	5.3571	2	0.06866
Clay	7.1353	2	0.02822
Organic	0.1696	2	0.9187
Elevation	1.1625	2	0.5592

Of the five key diatom species only *Navicula perminuta* recorded significant variance across the AHE ($P<0.05$) (Table 3.9).

Table 3.9: Kruskal-wallis analysis of variance on key diatom species

	H	df	p
Achnanthes clevei	5.18	2.00	0.08
Cocconeis placentula	1.33	2.00	0.51
Cocconeis scutellum var parva	0.94	2.00	0.63
Navicula perminuta	7.58	2.00	0.02
Nitzschia amphibia	2.18	2.00	0.34

3.10.2 Canonical Correspondence Analysis

Canonical Correspondence Analysis (CCA) was undertaken to determine how much influence specific environmental factors had over the distribution and abundance of the AHE diatom community and over the key diatom species. Of the environmental factors considered in this thesis MPI, silt, clay organic carbon and elevation were selected to determine the overall effect on diatom variance within the modern AHE.

Forty four percent of the total variance is accounted for when CCA is applied to the full data set (normalized individual species, not species assemblages) (Table 3.10). MPI correlates with individual species variance ($P<0.01$) as does silt and clay ($P<0.05$). Combined these three factors make up 31% or the recorded variance (Table 3.10) leaving 69% of the total variance unaccounted for.

Table 3.10: Canonical correspondence analysis of all diatom individual species, * = highly significant (0.001), ** = very significant (0.01), * = just significant (0.05).**

	H	F	Variance %
MPI	0.4114	0.010 **	10
Silt	0.4344	0.015 *	11
Clay	0.4132	0.020 *	10
Organic	0.2854	0.285	07
Elevation	0.2268	0.61	06

CCA was also undertaken on the key species, unfortunately none of the values provided by the key species CCA are significant. This indicated that in a modern setting the environmental factors selected in this thesis have no influence over the distribution of these species (Table 3.11, Figure 3.11).

Table 3.11: Canonical correspondence analysis of all key modern diatom species. * = highly significant (0.001), ** = very significant (0.01), * = just significant (0.05).**

	H	F	Variance (%)
Silt	0.1525	0.41	0.07
Clay	0.1063	0.54	0.05
Organic	0.0791	0.6	0.03
Elevation	0.2012	0.245	0.09
MPI	0.1054	0.415	0.05
Residual	1.6901		0.72

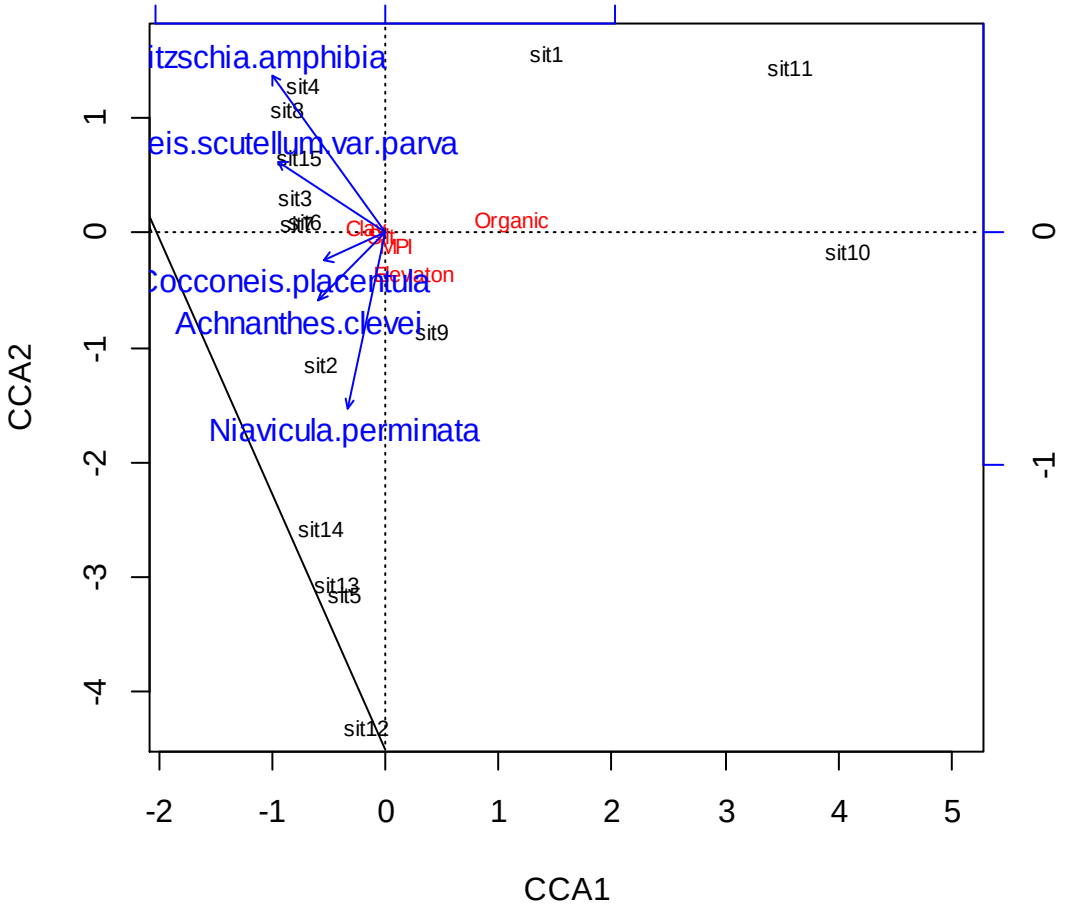


Figure 3.11: Canonical correspondence analysis of all key modern diatom species.

3.11 SUMMARY OF MODERN RESULTS

Five transect sites were established around the AHE, each transect was subsampled at sites relative to tidal height levels. Bridge St, Settlers Crescent and McCormacks Bay all exhibited an expected grain size distribution with coarser material being more abundant at higher elevations. The Southshore transect exhibited the reverse trend, and Moncks Bay recorded no identifiable trend. Organic carbon concentrations around the AHE were typically homogenous and low. However sample sites BSZ0, BSZ1 and McBZ1, had high concentrations. These sites had a soil component and a high abundance of both live and dead plant material present. Trace metal concentrations around the AHE are also relatively homogenous except for Pb concentrations in the Bridge St transect which exceed the ANZECC ISQG-Low guidelines for sediment contamination. Significant correlation exist between organic carbon and pollution indexes as well as between sediment grain size, PLI and MPI. Sediment grain sizes also correlates with organic carbon but no correlations exist between sample site elevation and any other environmental factor.

Dead species collected from surface samples around the AHE are shown to be an accurate representation of the living diatom community. Furthermore live vs dead diatom results show that the diatom community of the AHE have adjusted to the abrupt change in elevation brought about by the 2011 Christchurch earthquake.

Key diatom species and environmental factors record extremely limited correlations with only *Cocconeis scutellum var parva* correlating with elevation ($P<0.01$) and *Nitzschia amphibia* correlating with sediment grain size (sand and silt – $P<0.025$, clay – $P<0.01$). In terms of spatial diatom abundance or concentration change only *Navicula perminuta* and clay statistically differed between transect sites across the AHE.

CCA results indicate that statistically only 31% of total diatom species variance can be accounted for within the modern AHE (10% pollution, 11% silt and 10% clay). Interestingly a noticeable grouping of sample sites which were either closer to the Avon River or the Heathcote River was noted in the cluster analysis, indicating that river chemistry might have a level of influence species distribution and thus responsible for a portion of the remaining variance. Separate environmental influences which are not assessed in this study may also account for portions of the unaccounted 69% variance in the AHE. All raw data relevant to chapter 3 is provided in appendices A, B, C and D.

CHAPTER 4 – CORE RESULTS

4.1 INTRODUCTION

A single core from the Bridge Street transect area was collected on October 16th 2012 using an Eigenkamp Gouge auger. The site of core collection is found amongst thick patches of Jointed Sedge, near the Z4 sample site of the Bridge St transect (Table 4.1, Figure 4.1). Similar to chapter three, this chapter will identify changes in sediment composition, trace metal concentration and organic carbon concentrations as well as identify changes in diatom community structure through the BS core. Using statistical methods correlations between changes in environmental factors and diatom community structure will be identified and attempts to correlate changes in these environmental factors and historic events over the period of European colonization, industrial expansion and environmental remediation will be made. Additionally records of pre-European settlement diatom communities will be create which can be contrasted with modern diatom species and abundances to determine how large an effect the settlement of Christchurch has had on diatom species. All raw data associated with the results produced in this chapter will be provided in appendices E-G.

Table 4.1: Location, elevation, length and core labels given to cores collected from the Bridge St sample location.

	Core label	Core length (cm)	Latitude (S)	Longitude (E)
Bridge St	BSC-A BSC-B BSC-C	80 97 73	43°31’25.2”	172°43’30.4”

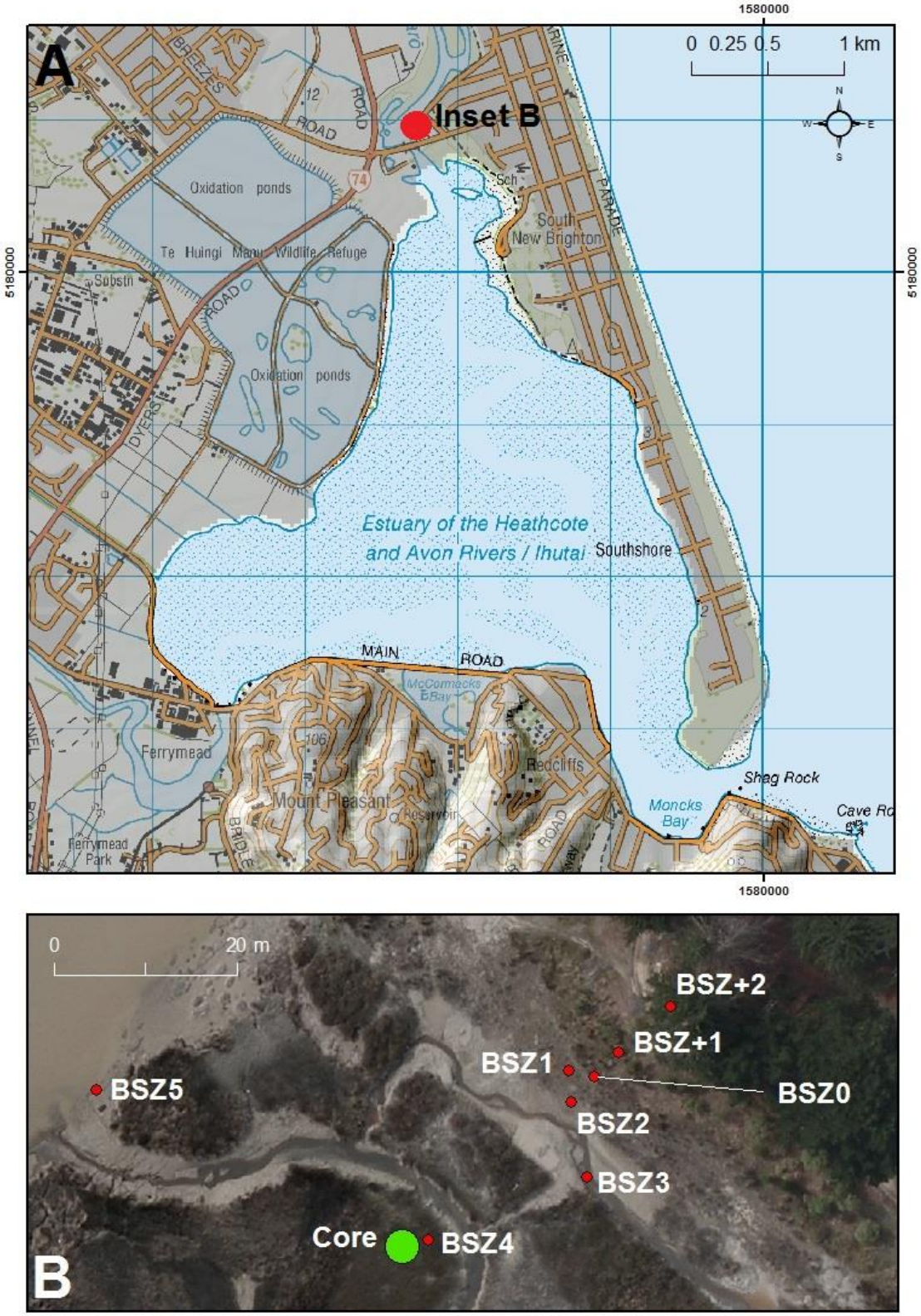


Figure 4.1 A & B: A - Road map of area surrounding the AHE with location of general area of Core sample zone. B – Close aerial image of the Bridge St transect with sites of transect sample sites in red and coring location in green.

4.2 CORE LOG

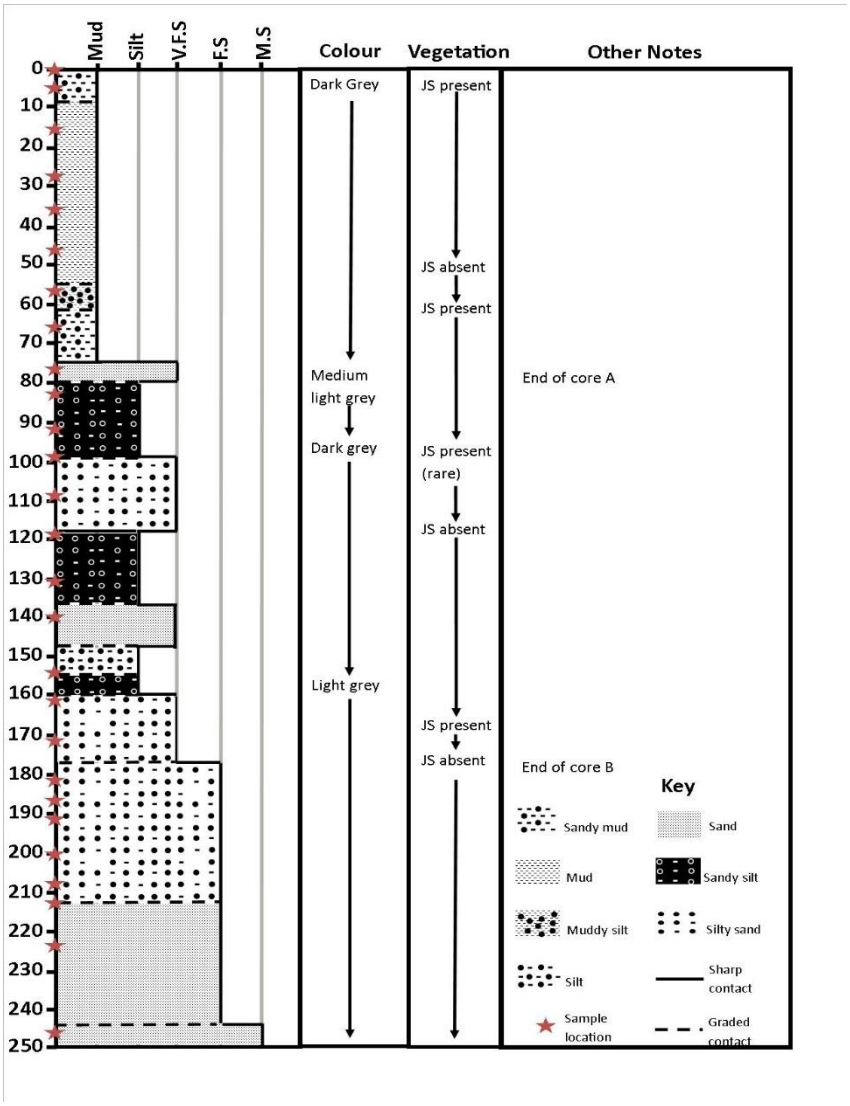


Figure 4.2: Core log of Bridge St core).

The core log (Figure 4.2) records a fluctuating environment where many small scale changes in both the dominant and subdominant grain size occur. The highest volume of coarse material is concentrated at the base of the core while all changes are gradational in nature. Jointed sedge vegetation (JE) becomes more frequent up core while the sediments move from dark gray-brown to grey brown in colouration in the middle of the core and back to a darker brown near the surface.

4.3 GRAINSIZE DISTRIBUTION

For accurate sediment measurements core samples were analysed using the Geological Sciences the Saturn digitizer II 5205 Laser Diffraction Spectrophotometer (details in methods), results produced from grain size analysis are provided in excel and PDF format and all relevant data is provided in appendix G. Limits for sand (above 63 microns), silt (between 63 and 3.9 microns) and clay (below 3.9 microns) were determined to best represent each section, and accumulative percentage of size class reported in grain size excel sheets were used to determine what proportions of each sample resided within our established grain size limits. A visual representation of grain size composition is given in figure 4.3.

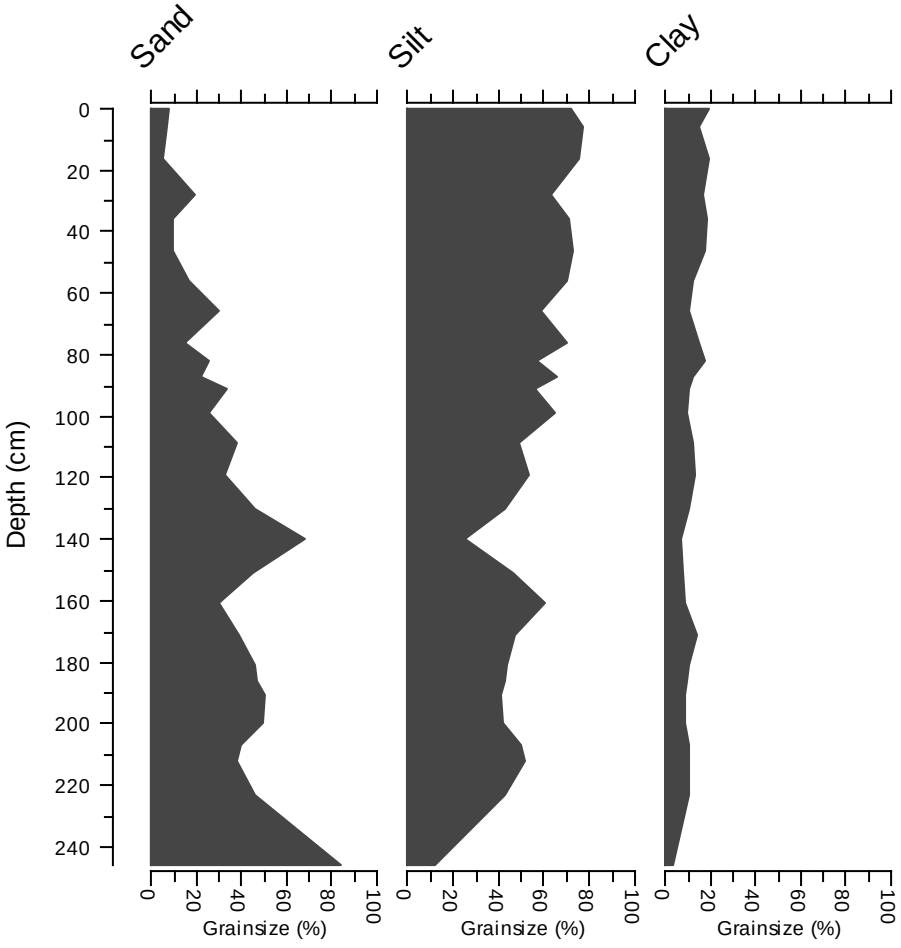


Figure 4.3: Reconstruction of grain size distribution through Bridge Street core. Representation is split into sand, silt and clay sized components.

4.3.1 Sand

The sand component of the Bridge St core indicates a decreasing trend in abundance from the base of the core to the surface. The highest reading is 83.8% at the core base and the lowest recorded percentage is 5.1% at 16cm. Five main peaks through the core are 50.4% sand at 191cm, 68% at

140cm, 30.2% at 66cm and 19.5% at 28cm below the core surface. The final stage of the core from 16-0cm a minor rise is recorded going from 5.1-8.4% (Figure 4.3).

4.3.2 Silt

Silt shows a gradual increase in grain size from the bottom of the core to the surface, starting at 12.3% at the base of the core, and has a steady increase to 51.9% by 212cm. A following peak of 60.8% is recorded at 161cm before a notable decrease to 25.2% at 140cm. From this point the increasing percentage of silt continues to a maximum of 77.4% at cm followed by a minor decrease to 72% at the core surface (Figure 4.3).

4.3.3 Clay

As with silt, clay also shows a gradual increasing trend in sediment proportions from the base of the core to the surface. Starting at 3.9% at the base five notable peaks are recognisable, 10.4% at 212cm, 13.8% at 171cm, 13.2% at 119cm, 17.3% at 82cm and 19.4% at 16cm. After this the core has a minor drop and ends at 19.6% at the core surface. A significant drop in clay percentage is recorded at 140cm with 6.8% of the total sample being clay (Figure 4.3).

4.4 GEOCHEMISTRY

Trace metals such as Nickel, Chromium, Copper, Zink, Iron and Lead which are targeted specifically from the AHE as they are known trace metal by products of the aforementioned activities and will best highlight anthropogenic input, additional trace metals (Arsenic, Cadmium, Cobalt and Manganese) have also been sampled. Graphic representations of concentration changes for each trace metal are provided in figure 4.4 a two tailed t-test of unequal variance has been undertaken for each trace metal to determine if concentrations of trace metals above 130cm (inferred European industrial initiation) have changed compared to below 130cm. This section is split into a description of the major points of concentration change for each individual trace metal of interest to this study.

4.4.1 Arsenic

Arsenic concentrations in the Bridge Street core sample variable on a minor scale, with multiple small spikes ad decreases in concentration. The highest concentration recorded is 11.4 mg/kg^{-1} at 56cm while the lowest is 2.9 mg/kg^{-1} at the very base of the core (246cm). Averages between samples recorded above 130cm (8.4mg/kg^{-1}) and below (4.9 mg/kg^{-1}) indicating enrichment, most likely from anthropogenic sources, the calculated percentage of enrichment between the lower and upper area is 71%. P-value of $3E^{-06}$ indicates a significant difference between the upper and lower section of the core.

4.4.2 Cadmium

Cadmium concentrations in the Bridge Street core of the AHE has extremely low values, with a minimum of 0.01 mg/kg^{-1} and a maximum of 0.6 mg/kg^{-1}. On a small scale concentrations of Cd do increase substantially compared to itself with an average concentration below 130cm of 0.04 mg/kg^{-1} and an average above 130cm of 0.27 mg/kg^{-1} with a calculated level of enrichment being 634%, P-value of these two sections equals 5E^{-05} indicating a significant difference between the two sectors.

4.4.3 Chromium

Chromium concentrations exhibit three major spikes throughout the Bridge Street core, 58.3 mg/kg^{-1} at 91cm, 60.5 mg/kg^{-1} at 82cm and 65.1 mg/kg^{-1} at 36cm. One major drop in Cr concentration is recorded at 76cm with 32.1 mg/kg^{-1}. Comparative measurements of Cr concentrations below 130cm and above 130cm record substantially differing averages, below 130cm equals 14.8 mg/kg^{-1} and above 130cm 46.1mg/kg^{-1} is recorded, this indicating an enrichment of 212%. P-values from t-tests indicate a significant difference between the two sections of core with a value of 2E^{-06}.

4.4.4 Cobalt

Cobalt shows a single concentrations spike, with the remaining values being variable but overall non-changing. The single spike occurs at 140cm with a concentration of 9.6 mg/kg^{-1}. The lowest value recorded for cobalt is 4.6 mg/kg^{-1} at the base of the core. Averages for cobalt concentration throughout the core show a reverse trend to what all other trace metals exhibit with a higher concentration seen below 130cm (67.2 mg/kg^{-1}) than above (6.6 mg/kg^{-1}) with a decrease in concentration of -9.5%. A P-value of 0.0717 indicates that although that no significant difference exists between the lower and upper section of the core for cobalt.

4.4.5 Copper

Copper concentrations record show three spikes of interest, 33.5 mg/kg^{-1} at 91cm, 33.7 mg/kg^{-1} at 56cm and 37.1 mg/kg^{-1} at 36cm respectively. A minor concentration drop is recorded at 66cm with 26.7 mg/kg^{-1}, which coincides with an overall trace metal concentration drop at this stage of the core, but is not a pronounced as Cr, Ni or Pb. A t-Test was performed to establish if a statistically significant difference was seen in concentrations recorded below and those recorded above 130cm, the P-value from was recorded at 1E^{-07} and thus was proven to be statistically different. The average concentration from below 130cm is 7.4 mg/kg^{-1} and the average for samples above was 27.7 mg/kg^{-1}, increasing concentration of 274%

4.4.6 Lead

Lead records four major concentration spikes, happening at 99cm (75.9 mg/kg^{-1}) 82cm (75.2 mg/kg^{-1}), 56cm (84.1 mg/kg^{-1}) and 36cm (88.3 mg/kg^{-1}). As with Cr and Ni a significant reduction in trace metal concentration is recorded at 76-66cm (lowest of 59.1 mg/kg^{-1}). A major change in concentration values occurs at 130cm with Pb concentrations above this point being substantially higher (average of 62.1 mg/kg^{-1}) than samples recorded below it (average of 15.5 mg/kg^{-1}) resulting in a concentration increase of 301%. T-test P-value of 5E^{-07} shows that there is a significant difference between the two sections of the core.

4.4.7 Manganese

Manganese concentrations exhibit two spikes of importance and one decrease in concentration. Spikes occur at 76cm (261.4 mg/kg^{-1}) and 16cm (298.7 mg/kg^{-1}) with the decrease in concentration at 46cm recording 229.6 mg/kg^{-1}. Averages for above the 130cm mark equal 251.8 mg/kg^{-1} while those below are over 10% smaller with an average of 214.4 mg/kg^{-1}. Between the two areas a recorded increase of 17.5% is seen in trace metal concentrations. The P-value from the T-test analysis result in a 0.0001, indicating that the changes seen above and below 130cm are significant.

4.4.8 Nickel

Nickel concentrations exhibit three major spikes throughout the Bridge Street core, 17.3 mg/kg^{-1} at 91cm, 17.1 mg/kg^{-1} at 82cm and 18 mg/kg^{-1} at 36cm. One major decrease at 76cm where concentrations reached 14.7 mg/kg^{-1}. Trace metal concentrations below 130cm change substantially when compared to concentrations recorded about 130cm with samples below 130cm having a lower concentration than those above. The average for trace metal samples below 130cm is recorded as 12.4 mg/kg^{-1}, while those above are 15.7 mg/kg^{-1}, this means that a 27.5% increase in concentration is recorded. T-test correlations between these two sections produce a P-value of 8E^{-06} indicating a significant difference between both sections of core.

4.4.9 Iron

Iron has a substantially higher concentration than any other trace metal in this study but still follows a similar pattern in concentration increases and decreases that has been shown in other studied trace metals for the AHE. From the base of the core concentrations fluctuate but follow a generally decreasing trend to 130cm depth (14271 mg/kg-^{1}) From 130cm to 16cm (24271 mg/kg-^{1}) depth a gradual increase in concentration is recorded, again fluctuations are seen but they are not major changes. From 16cm to the core surface Iron concentrations decrease again.

4.4.10 Zinc

Zinc trace metal concentrations vary significantly to Cr, Ni, Cu and Pb. Three significant spikes are recorded, these being at 109cm (186.7 mg/kg^{-1}), 76cm (193.1 mg/kg^{-1}) and 36cm (256.1 mg/kg^{-1}). The second spike (76cm) coincides with recorded concentration drops in other recorded trace metals and a decrease in Zn concentrations at 99cm coincides with a spike in other trace metals. An average of 51.5 mg/kg^{-1} is recorded below 130cm and above the average is substantially higher with 157mg/kg^{-1} indicating a 205% increase in concentration between areas. These differences are proven to be statistically significant with a P-value of 6E^{-07}.

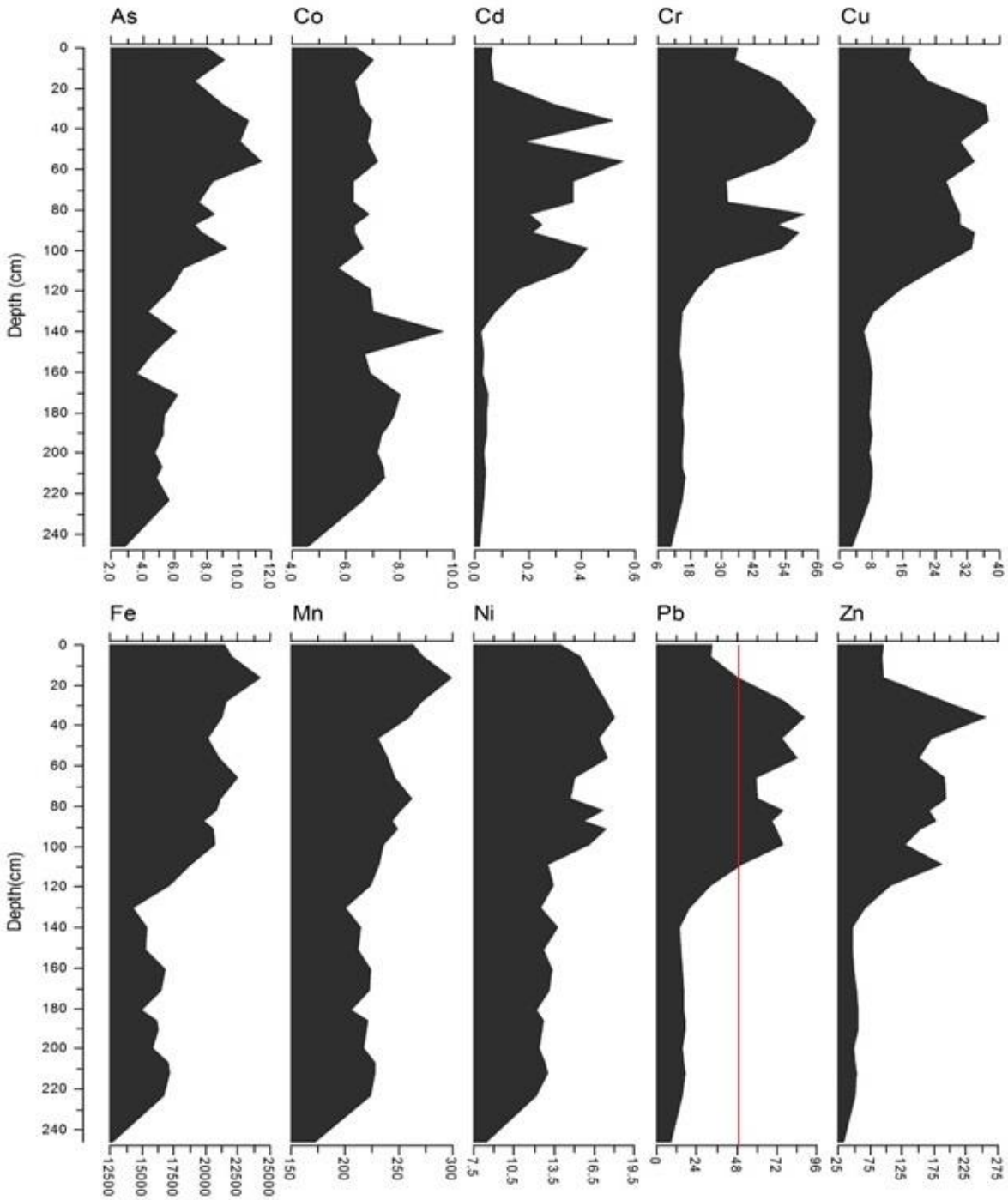


Figure 4.4: Reconstruction of trace metal concentration changes as recorded in the Bridge St core. Results are recorded in mg/kg^{-1} large spike in concentrations recorded at 130-140cm depth below the core surface. Red vertical bars indicate ANZECC ISQG-Low trigger values, only Pb concentrations record higher values than the guidelines.

4.4.11 Summary

Two distribution patterns for the trace metals were identified within the sediment profile. Trace metals As, Cd, Cr, Cu, Pb, Mn, Ni, Fe and Zn are all enriched above 130cm, Levels of concentration enrichment vary between trace metals, where the most enriched was 63.4% (Cd) and the least was 17.4% (Mn). Below 130cm all trace metals, apart from cobalt, have a concentration which is substantially lower and much less variable than the concentrations recorded above 130cm. This is a trend that is reflected multiple locations around New Zealand, a study by Dickinson et al., 1996 identified that trace metal concentrations in Wellington Harbour (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb and Zn) loosely reflect those seen in the AHE cores. Each trace metal in the Dickenson study records a stable low concentration period near the base of the core, followed by a concentration spike in the upper 100cm. Similarly Abrahim and Parker (2002), looked specifically at Cd, Cu, Pb and Zn in the Tamaki Estuary or Auckland. As with our studies and those of Dickenson et al. (1996) and Abrahim and Parker (2002) show that significant enrichment of trace metals has occurred in the upper portion of the cores. Notably trace metal spikes in New Zealand tend to be confined to the upper 100 or less cm of cores, where in the samples from the AHE these spikes generally occur at 130cm, with elevated levels of trace metals to ~40cm depth. Worldwide a similar trend where trace metal concentrations suddenly increase sediments from estuaries, harbours, lakes and rivers which are subjected to intensive periods of industrial activity over recent history (Li et al. 2007; Le Cloarec et al. 2011; Morelli et al. 2012; Thevenon et al. 2011)and has been related to be caused by dominantly anthropogenic process in most cases. As heavy industrial activity occurred in Christchurch earlier than Wellington or Auckland it is unsurprising that trace metal concentrations increase at greater depth than those recorded by Dickenson et al. 1996 or Abrahim and Parker. (2002).

In the upper 40cm of the Bridge St core all trace metal concentrations decrease noticeably (excluding cobalt), this trend is also seen in the work by Dickinson et al. 1996 and Abrahim and Parker (2002) for Wellington harbour and Auckland estuary in New Zealand. In general this trend is also seen in other studies worldwide where industrial activity has occurred and is thought to coincide with increasing environmental awareness through the 1960-80's. A trend that differs to studies in other areas around New Zealand is the minor concentration increase seen in the sediment immediately below the cores surface in Cd, Cr, Cu, Pb and Zn. An interesting trend which could in part be a reflection of reworked sediment, external influence of the recent Canterbury earthquakes or inputs from waste water outfall.

4.5 POLLUTION INEDXES

Pollution indexes all show similar trend and closely reflect trends shown in individual trace metals. MPL and mC_d start with relatively low index numbers at the base of the core, and no substantial change is observed from the base to 130cm (Figure 4.5). From 130cm to 36cm (highest index levels) depth two major spikes are recorded, a sharp rise in index numbers from 130cm to 99cm if the first, which is likely coinciding with European settlement, the second spike occurs at 56cm. From 16cm depth to the core surface a sharp decrease in index levels can be seen.

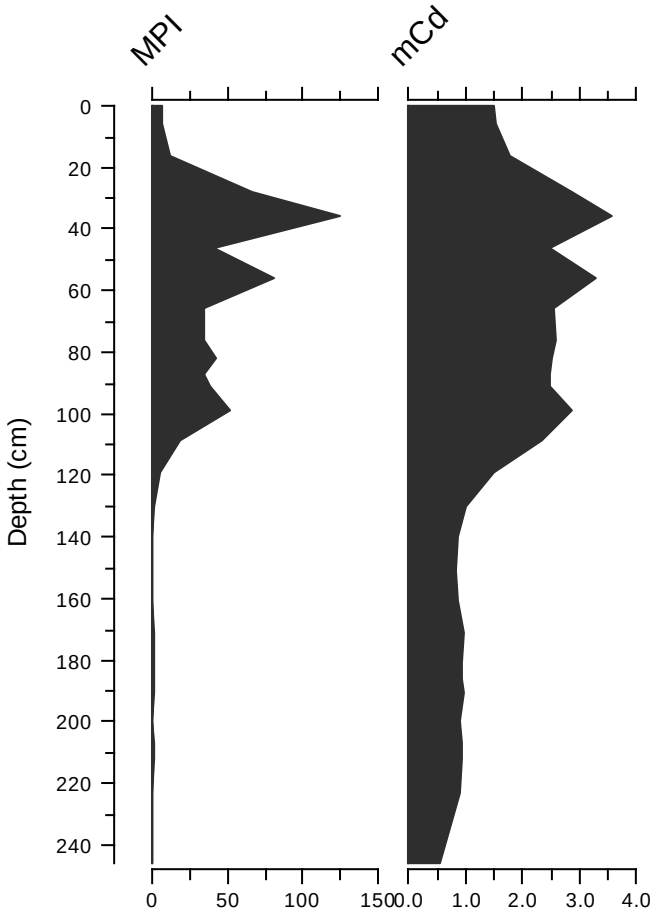


Figure 4.5: Graphic representation of chances of the MPL and mC_d from the surface to the base of the AHE core.

4.6 ORGANIC CARBON

Organic carbon in the AHE core follows similar trends to trace metal profiles. Below 140cm organic carbon concentration varies hardly at all, with a maximum of 0.5% and a minimum of 0.14% of the total sample. Above 140cm concentration of carbon does fluctuate, three main peaks are recorded at 109cm surface, 87cm and 56cm making up 1.21, 1.89 and 2.79% of the total sample. Between 140cm and 16cm over all organic carbon concentrations increase, once at 16cm a gradual decrease in concentration from 2.31% to 1.95% at the sediment surface (Figure 4.6).

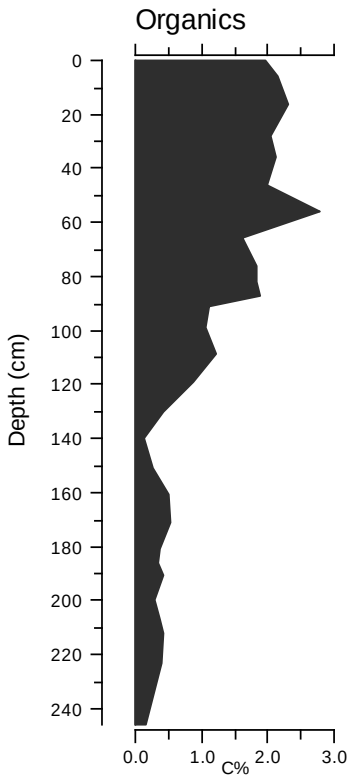


Figure 4.6: Organic carbon profile for the Bridge St core of the AHE.

4.7 CAESIUM 137 DATING

Caesium 137 dating indicated that the radioactive spike associated with nuclear testing in the 1950's is located between 56cm and 66cm (Table 4.2). As ^{137}Cs is below the detection limit in sample 66cm and 140cm, the first appearance of ^{137}Cs seems to be between 66 cm and 58 cm. The spectrum for 91.5cm shows a tiny ^{137}Cs peak but the activity but it is indistinguishable from zero if 2 sigma errors are assigned.

Figure 4.2: ^{137}Cs dating results on core sediments

Depth (cm)	Weight in vial (g)	^{137}Cs activity ($Bq.kg^{-1}$)
28	4.40	1.50 ± 0.33
46	4.40	1.35 ± 0.31
56	4.40	1.83 ± 0.36
66	5.24	-0.10 ± 0.24
91.5	5.24	0.65 ± 0.27
140	6.45	-0.27 ± 0.24

4.8 AGE PROFILE

MPI, organic carbon, silt and clay have been graphed together to create a age profile of the Bridge St core. With ^{137}Cs dates being established and plotted on top of core profiles for the aforementioned factors (Figure 4.7) this study has then inferred the depths which would likely represent important events in the history of European occupation of the AHE. These date location have been selected as likely places due to the expected changes in pollution which each event would incur and in relation to the known ^{137}Cs location.

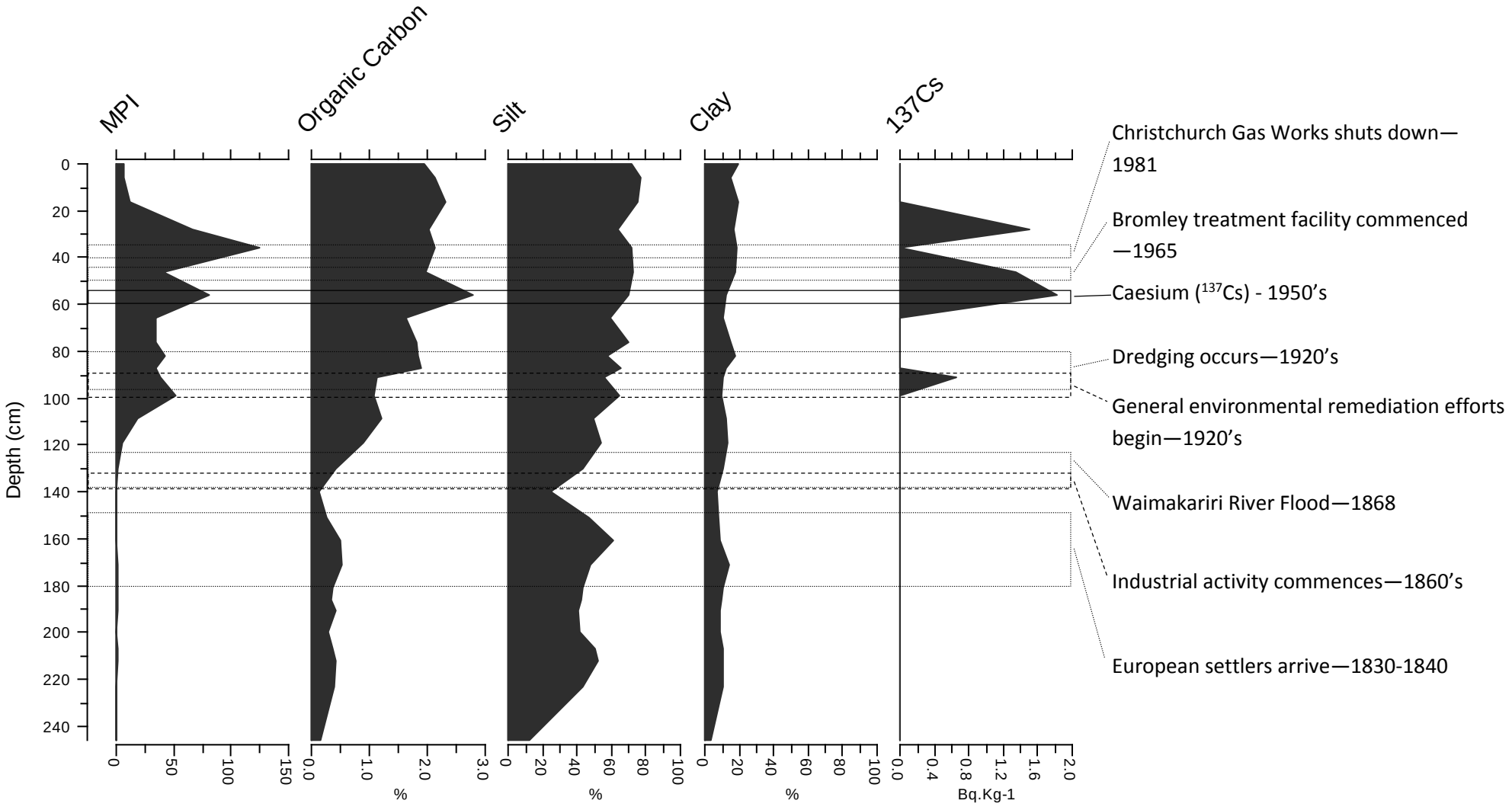


Figure 4.7: Age profile of historic events relative to environmental fluctuations. Solid lines indicate certain age brackets for events, broken lines indicate inferred location of events relative to environmental fluctuations and known events.

4.9 ENVIRONMENTAL CORRELATIONS

Spearman's correlation coefficient was undertaken on all environmental data collected from the BS core to assist in determining correlations between environmental factors. Every single environmental factor, including individual trace metals with the exception of cobalt correlated with each other (P<0.001) (Table 4.3). Organic carbon, MPI, PLI, mCd, silt and clay all indicated positive correlations while sand has the inverse.

Table 4.3: Spearman's correlation coefficient results between environmental factors. * = highly significant (0.001), ** = very significant (0.01), * = just significant (0.05)**

	Sand	Silt	Clay	MPI	mCd	Carbon
Sand	1.00					
Silt	-0.99***	1.00				
Clay	-0.83***	0.78***	1.00			
MPI	-0.72***	0.71***	0.70***	1.00		
mCd	-0.70***	0.69***	0.67***	0.98***	1.00	
Carbon	-0.92***	0.90***	0.86***	0.85***	0.83***	1.00

4.10 DIATOM ASSOCIATIONS

Seventy seven diatom species were identified from samples out of the Bridge Street core, 45 of which were considered viable to use in statistical analysis (remaining 32 species identified occurred in to small an amount to be considered relevant). All up over 1700 separate diatom valves were counted and identified. Raw data was collected as counts of 100 valves, due to the large volume of material raw data was normalised to 100% for analysis in C2 and PAST. A total of 90 taxa were recorded although some taxa were only recorded a few times. To improve the data analysis in C2 and PAST raw data species with total counts of less than 3% of the sampling size (100 species per sample) were removed. Diatom species and sample assemblages were developed by running cluster analyses in PAST statistical software. Cluster analysis organises data into clusters (or groups), in the case of this project, distinct clusters of similar diatom taxa and clusters of similar collection sample zones. Species/samples in each assemblage are more similar with each other in some way than with species/samples residing in other assemblages. To produce dendrogram classifications of samples (cluster analysis) 2-way Bray-Curtis distance matrix was used (Figure 4.8).

4.10.1 Diatom species associations

Species Assemblage 1

Species: *Gomphonemopsis* sp1*, Achnanthes brevipes* (BM), *Hantzschia amphioxys* (FB), *Navicula recens* (FB).

Dominant sample association: G

Secondary sample associations: D

This association is most abundant in the upper most section of the core where trace metals are at their lowest since European settlement and generally have low sand concentrations.

Species Assemblage 2

Species: *Nitzschia* sp3*, Fragilariopsis* sp1*,* Navicula *cryptotenella* (F), *Diploneis smithii* (B), *Navicula incertata* (F).

Dominant Sample Association: B

Secondary sample associations:

Species association 2 is most abundant in samples with low sand percentages (slightly sandy muds) as well as high trace metal concentrations.

Species Assemblage 3

Species: *Navicula* sp4*, Planothidium linkei* (F), *Nitzschia inconspicua* (FB), *Grammatophora hamulifera* (M), *Opephora* sp1*, Cocconeis peletoides* (BM), *Birenuis lucens* (BM), *Thalassiosira* sp1*, Achnanthes coffeaeformus* (BF).

Dominant sample association: D

Secondary sample association: E

This association is common in samples with low trace metal concentrations and prefers sample sites with low sand (slightly sandy muds) but is recorded muddy sand samples as well.

Species Assemblage 4

Species: *Achnauthidium rivulare, Achnanthes brevipes var intermedia* (BM)

Dominant sample association: C

Secondary sample association: none.

This association is low in abundance throughout the core (1-3% of total diatoms per sample). It is most abundant in samples with moderate sand components (very sandy muds) and is recorded in samples with high trace metal concentrations.

Species Assemblage 5

Species: *Opephora pacifica* (M).

Dominant sample association: D

Secondary sample association: none.

This association is only present at a single location where both sand percentage and trace metal concentration are low.

Species Assemblage 6

Species: *Navicula* sp3*, Achnanthes lanceolata* (FB), *Opephora marina* (M).

Dominant sample association: C

Secondary sample association: B

This association is extremely abundant in areas with moderate sand percentages (sandy muds) and moderate to high trace metal concentrations.

Species Assemblage 7

Species: *Cocconeis placentula* (F), *Opephora guenter-grassii* (BM), *Pseudostaurosira* sp1*, Cocconeis sublittoralis* (BM), *Navicula perminuta* (B), *Nitzschia amphibia* (F), *Cocconeis scutellum var parva* (BI), *Achnanthes clevei* (F).

Dominant sample association: Common in all sample associations

Secondary sample association: none.

This entire association is seen throughout the core where diatoms were recorded. No preference to trace metal concentration or grain size components can be seen.

Species Assemblage 8

Species: *Grammatophora* sp1*, Pseudostaurosire parasitica* (F), *Navicula delicatissima* (M).

Dominant sample association: A

Secondary sample association: F

This association represents areas with high sand proportions (muddy sands and very sandy muds) with low trace metal concentrations.

Species Assemblage 9

Species: *Fragilaria brevistriata* (FI), *Fragilaria* sp1*, Nitzschia granulate* (BM), *Opephora* sp2*, Nitzschia compressa* (BM), *Eunoypgramma marinum* (BM).

Dominant sample association: B, F

Secondary sample association: none.

This association is most abundant in locations with both moderate to low trace metal concentrations and sand percentages. This association becomes rarer in areas with very low or very high trace metal concentrations.

Species Assemblage 10

Species: *Nitzschia hungarica* (FB), *Achnanthes* sp1*, Fragilaria* sp2*, Gomphonemopsis* sp3.

Dominant sample association: E

Secondary sample association: none

This association is most common in high trace metal concentrations and low to moderate sand percentages (mud-sandy mud).

4.10.2 Diatom sample associations

Sample Assemblage A:

Samples: 181-183

Dominant species association: 7, 6

Secondary species associations: 3, 8, 9

Sediment: muddy sand

Diversity indices: α=0, H= 2.203, E= 0.6961

Summary: This association is comprised of only one sample and is found in muddy sands with low trace metal concentrations. A low to moderate preservation of diatom valves is recorded for this association as well as a low diversity. This association is dominated by *Achnanthes lanceolata* (24% abundance) and *Cocconeis scutellum var parva* is sub-dominant (16% abundance). This association occurs in muddy sands with low trace metal concentrations at only one point in the Bridge St core.

Sample Assemblage B:

Samples: 66-68, 82-84, 99-101, 76-78, 87-89, 130-132

Dominant species association: 10, 9

Secondary species associations: 1, 2, 3,8, 9, 10

Sediment: sandy mud

Diversity indices: H=0.9743 – 2.387, E=0.58-1

Summary: This association is comprised of six samples, all of which are found in sandy muds with moderate to high trace metal concentrations. Diatoms preservation is low to moderate but with a high

diversity. This association is dominated by *Achnanthes clevei* (21.2% mean abundance) and *Cocconeis placentula* is sub dominant (19.3% mean abundance).

Sample Assemblage C:

Samples: 109-111, 119-121

Dominant species association: 6

Secondary species associations: 2, 7, 8, 9

Sediment: sandy mud

Diversity indices: H= 0.6365-2.954, E= 0.4821-0.9811

Summary: This association is comprised of two samples, both of which are found in sandy muds with moderate to high trace metal concentrations (trait 2 peaks for Zn and Pb). Diatom preservation is low to moderate and diversity is moderate and are dominated by *Navicula* sp2 (23% mean abundance) and *Achnanthes lanceolata* and *Achnanthes clevei* are co-sub dominate (16.5% mean abundance).

Sample Assemblage D:

Samples: 0-2, 16-18, 186-189,193-196

Dominant species association: 3, 7

Secondary species associations: 1, 2, 5, 6, 9, 10

Sediment: mud and muddy sand

Diversity indices: H= 0-2.954, E= 0.4821-1

Summary: This association is comprised of four samples, all of which display low trace metal concentrations, 0-2 and 6-8 consist of mud will less than 8.5% sand while 186-189 and 193-196 represent muddy sands. Moderate diatom preservation and diversity is recorded in 0-2 and 6-8 but 186-189 and 193-196 both have low diversity and low preservation. This assemblage is dominated by *Navicula perminuta* (20.6% mean abundance) and *Cocconeis placentula* is sub-dominant (18% mean abundance).

Sample Assemblage E:

Samples: 36-38, 46-48, 56-58, 91.5-93.5

Dominant species association: 7, 10

Secondary species associations: 1, 3, 4, 8, 9

Sediment: mud, sandy mud and very sandy mud

Diversity indices: H=0.4506-2.954, E= 0.4821-0.9802

Summary: This association is comprised of four samples, all of which display extremely high concentrations of trace metals (36-38, 46-48, 56-58 all cover the trait 2 peak, and each zone covers

the trait on peak for all trace metals apart from Zn). 36-38, 46-48 consist of mud (<9.7% sand), 56-58 consists of sandy mud (17.1% sand) and 91.5-93.5 consists of very sandy mud (33.3% sand). Samples are moderate to low in both diversity and preservation, furthermore this association is dominated by *Cocconeis scutellum var parva* (14.5% mean abundance) and *Nitzschia amphibia* is sub-dominant (13.8% mean abundance).

Sample Assemblage F:

Sample: 28-30

Dominant species association: 9, 10

Secondary species associations: 3, 4, 6, 8

Sediment: sandy mud

Diversity indices: H= 0.6902-2.954, 0.4821-0.9589

Summary: This association is comprised of one sample with a grain size representing sandy mud and moderate to trace metal concentrations. Moderate diatom preservation is recorded but diversity is low. The dominant species for this association is *Cocconeis scutellum var parva* (19% abundance) and *Navicula perminuta* is sub-dominant (11% abundance).

Sample Assemblage G:

Sample: 6-8

Dominant species association: 1, 7

Secondary species associations: 2, 9

Sediment: mud

Diversity indices: H= 0-2.954, E- 0.4821-1

Summary: This association is comprised of one sample with grain size of mud and low trace metal concentrations. Moderate diatom preservations is recorded and the sample is low in diversity. This association is dominated by *Cocconeis scutellum var parva* (16% abundance) and *Gomphonemopsis sp1* is sub-dominant (14% abundance).

Sample Assemblage H:

Sample: 207-210

Dominant species association: 7

Secondary species associations: 6

Sediment: muddy sand

Diversity indices: H= 1.494-2.804, E= 0.6365-0.8258

Summary: This association is comprised of one sample with a grain size of muddy sand, it also has low trace metal concentrations additionally diatom preservation and abundance are extremely low. This association is co-dominated by *Achnanthes clevei* and *Navicula perminuta* (33% abundance) while *Opephora marina* and *Pseudostaurosira* sp1 are co-sub-dominant (17% abundance).

Sample Assemblage I:

Sample: 171-173

Dominant species association: 7

Secondary species associations: 8

Sediment: muddy sand

Diversity indices: H= 1.507-2.954, E= 0.4821-0.9589

Summary: This association is comprised of one sample with a muddy sand grain size and a low concentration in trace metals. Diatom diversity and preservation are extremely low, furthermore this association is dominated by *Opephora guenter-grassii* (50% abundance) while *Cocconeis placentula, Cocconeis sublittoralis, Pseudostaurosira* sp1 and *Grammatophora* sp1 all co-subdominate this sample (13% abundance).

4.10.3 Core species and site assemblage summary

Site assemblages B, C and E appear to group sample sites in accordance with areas of increased levels of pollution (>4.72 (PLI), >0.62 (MPI) and >0.90(mC_d)). The maximum and minimum pollution values established by pollution indexes in the core are 125.32 (MPI) and 1.09 (MPI). Site assemblage D (sample sites 0cm, 16cm, 186cm and 193cm)consists of sample sites located at both the very top and the near the base of the core. The lower section of the core corresponds with the lowest MPI pollution values (186cm – 0.81, 193cm – 0.84) and pollution values corresponding with site assemblage D in the upper sections show a decreasing trend (0cm – 6.29, 16cm - 12.17). The remaining site assemblages (A, F, G, H and I) are all composed of a single sample site. Aside from having a differing composition of species diversity and abundance from site assemblages B, C, E and D no other conclusions can be drawn.

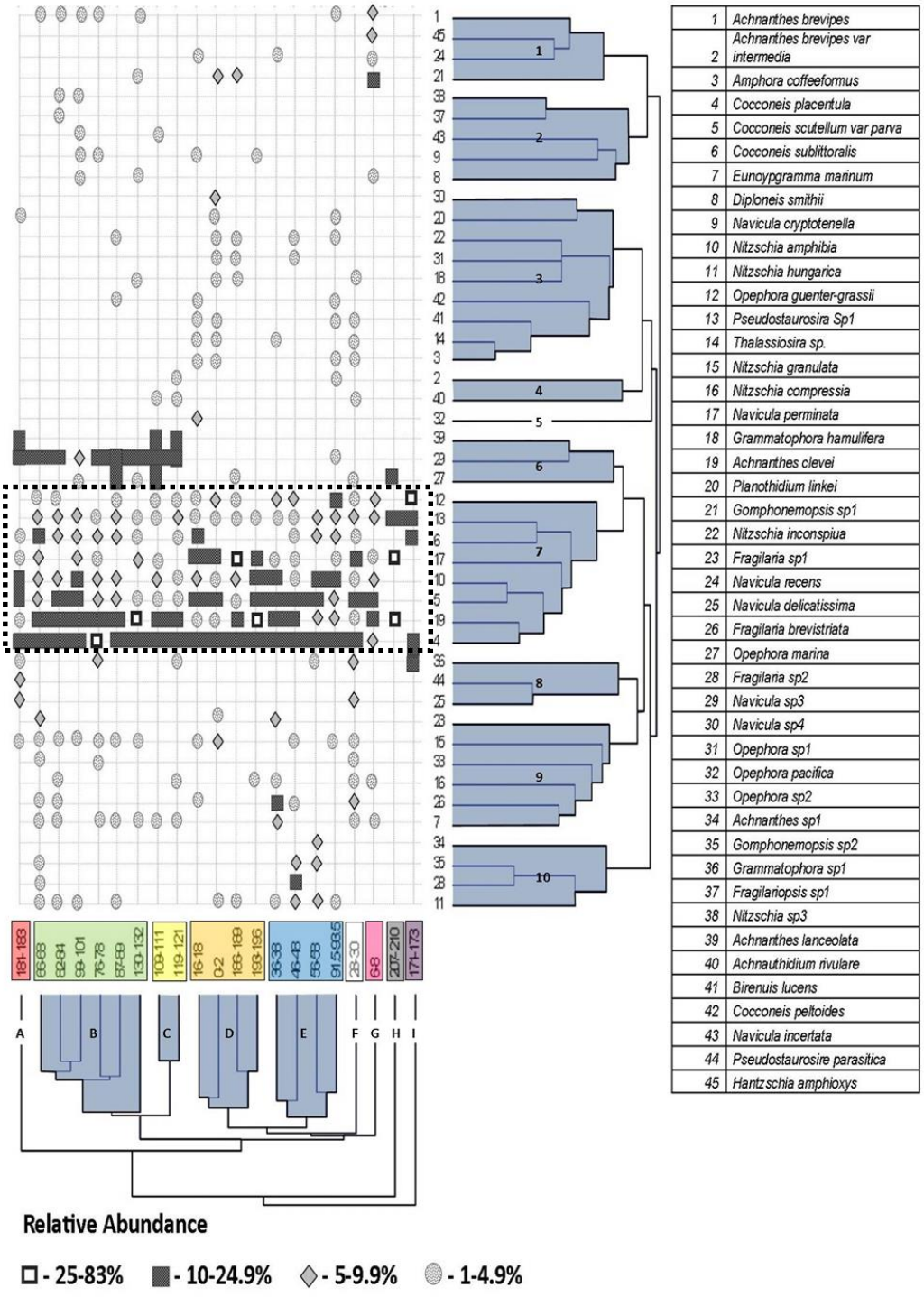


Figure 4.8: Core diatom associations in the AHE, New Zealand. Ten distinct species associations and 9 distinct site associations developed when Bray-Curtis distance matrix is used to produce dendrogram classifications.

4.11 ASSEMBLAGE PROFILE

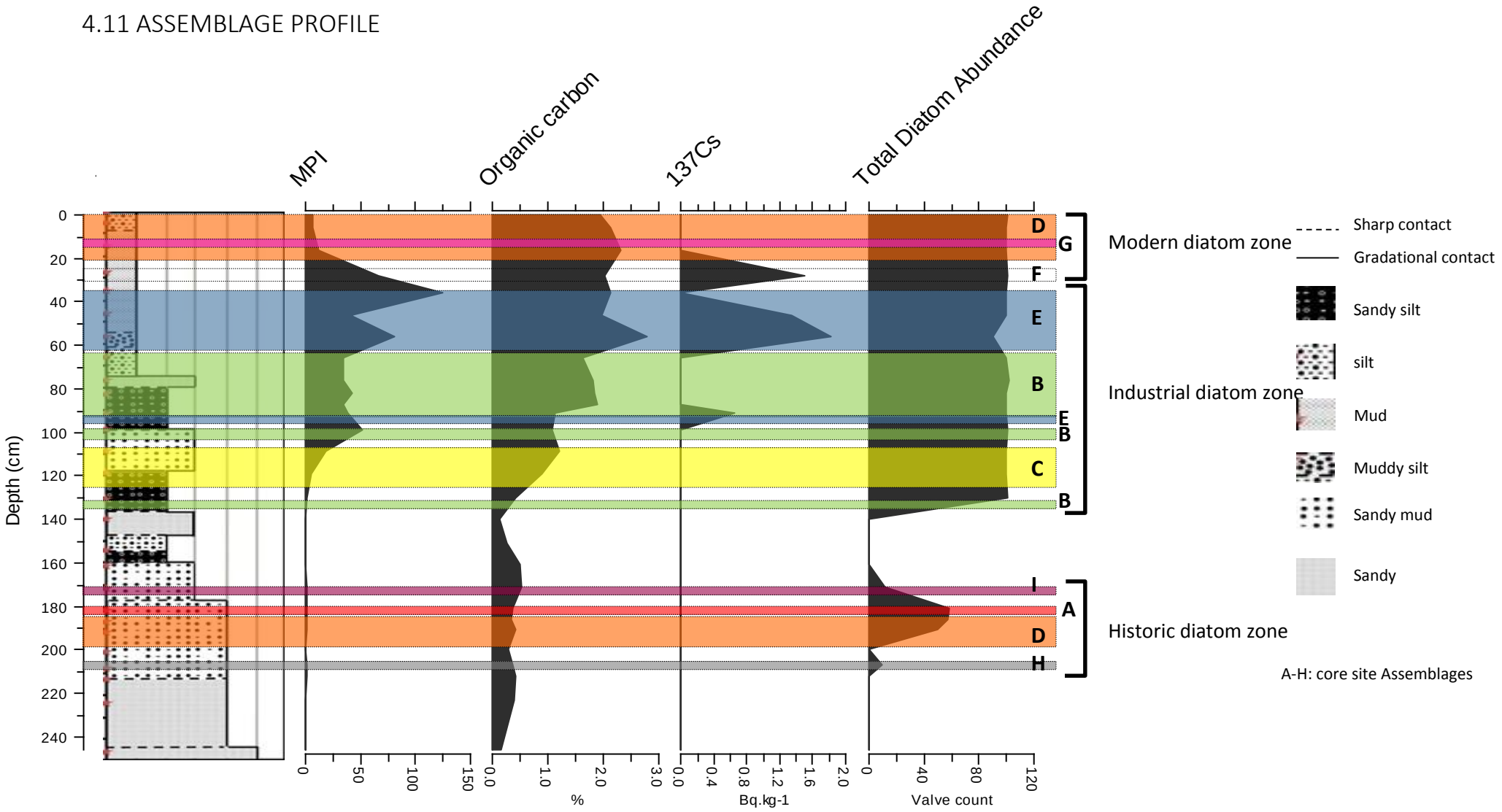


Figure 4.9: Assemblage age profile indicating where assemblages occur relative to changes in trace metal, organic carbon, caesium 137 and grain size changes.

Three distinct sections in the AHE core are established by the assemblage profile (Figure 4.9). The first of which is a modern section (0cm – 30cm) where all sediment samples post-date the last major source of effluent discharged into the AHE (Christchurch Gas Works). The second, an industrial section (36cm – 142cm) which encompasses the section of core which was most heavily subjected to industrial waste. Finally a natural section (151cm – 248cm) which is comprised of samples taken from the core which pre-date the industrial period of New Zealand.

In the historic zone site assemblages A, D and I are present, progressing up the core the sample assemblages change within the industrial zone to B, C and E. Transitioning into the modern zone brings a complete a complete change in sample assemblages present, assemblages B, C and E vanish, sample assemblage D re-appears and sample assemblages F and G appear for the first time.

The major point which can be pulled out of figure 4.9 is that sample assemblage D is found in both the modern and historic zones. Additionally sample assemblages B, C and E are confined to the industrial zone. This difference indicates that not only is activity occurring during the industrial period noticeably changing the diatom community composition found in associated industrial samples, but also, post environmental remediation efforts have allowed diatom community composition to return to a state similar to what it was pre-industrial activity.

4.12 DIATOM AND ENVIRONMENTAL CORRELATIONS

Spearman's ranked correlation was also utilized when comparing environmental factors and key diatom species. All key species correlate to some degree with the selected environmental factors. *Navicula perminuta* and *Achnanthes clevei* correlate with pollution indexes ($P<0.05$ and 0.001 respectively) as well as organic carbon ($P<0.05$). *Cocconeis placentula* and *Nitzschia amphibia* correlate with pollution indexes and organic carbon ($P<0.001$), as well as sand, silt ($P<0.01$) and clay ($P<0.05$). *Cocconeis scutellum var parva* records correlations with all environmental factors with a p-value of 0.001. The results for the aforementioned correlations can be viewed in table 4.4 below.

Table 4.4: Spearman's ranked correlation of key core diatom species and environmental factors.

	Cocconeis placentula	*Cocconeis scutellum var parva*	*Nitzschia amphibia*	*Navicula perminuta*	*Achnanthes clevei*
Sand	-0.58**	-0.80***	-0.52**	-0.34	-0.36
Silt	0.58**	0.78***	0.52**	0.34	0.38
Clay	0.57*	0.71***	0.43*	0.34	0.35
MPI	0.70***	0.80***	0.78***	0.41*	0.61***
mCd	0.74***	0.77***	0.81***	0.40*	0.64***
Carbon	0.62***	0.86***	0.64***	0.39*	0.44*

4.13 ENVIRONMENTAL AND DIATOM CHANGE

4.13.1 Environmental change

To determine whether environmental factors or key diatom species have changed over the depositional period of the Bridge St core (~200 years) statistically Kruskal-Wallis analysis of variance has been used. This study found that all environmental parameters used to determine influences acting on diatom species recorded significant change through the three established modern, industrial and historic areas of the core (Table 4.5), critical values outlined in table 2.1.

Table 4.5: Kruskal-Wallis analysis of variance on environmental factors recorded in the AHE core.

	H	**df**	**p-value**
Carbon	16.4047	2	0.000274
Silt	13.8773	2	0.00097
Clay	13.2623	2	0.001319
MPI	15.8727	2	0.000358

4.13.2 Diatom change

Four out of the five key diatom species in the AHE core a significant level of change between the modern, industrial and natural core sections (Table 4.6). This indicates that over the last 200 years some influence, likely associated with anthropogenic activity, has changed the abundance of these four key species.

Table 4.6: Kruskal-Wallis analysis of variance of key core diatom species recorded in the AHE core.

	H	df	p
Achnanthes clevei	11.6693	2	0.002924
Cocconeis placentula	11.8103	2	0.002725
Cocconeis scutellum var parva	11.6372	2	0.002972
Navicula perminuta	5.8709	2	0.05311
Nitzschia amphibia	6.0775	2	0.0479

4.13.3 The effect of environmental factors on Diatom variation

Using CCA the environmental factors selected to compare with variation seen within the total diatom community indicated that they had minimal influence on diatom variance. The results indicate that of the accounted variance statistically only 8% (MPI) can be accounted for ($P<0.05$), leaving the remaining 92% unaccounted for (Table 4.7).

Table 4.7: Canonical correspondence analysis of all core diatom species and selected environmental factors.

	Chisq	Pr(>F)	variance %
Clay	0.1238	0.12	0.07
MPI	0.1557	0.035 *	0.08
Organic	0.1165	0.225	0.06
Silt	0.0758	0.785	0.04

As with the CCA analysis of key species in the modern setting when CCA was applied to the key diatom species in the core no significant correlation between them and the environmental factors were recorded (Table 4.8). Figure 4.10 depicts a CCA plot for visual analysis of the effects of environmental factors on each key species and sample sites.

Table 4.8: Canonical correspondence analysis of all key core diatom species and selected environmental factors.

	H	F	Variance (%)
Silt	0.0427	0.09	0.04
Clay	0.017	0.4	0.02
Organic	0.0111	0.605	0.01
MPI	0.028	0.245	0.02
Residual	1.0307		0.91

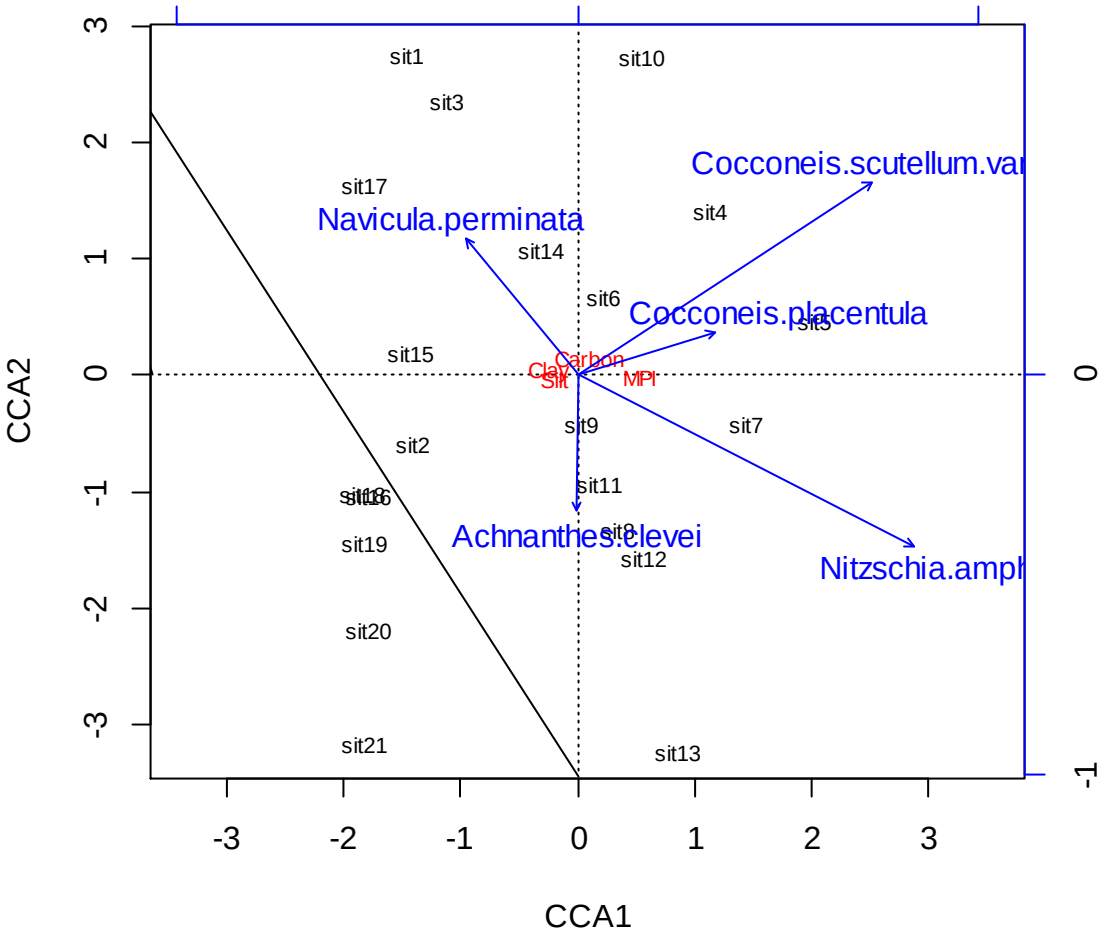


Figure 4.10: CCA plot of key diatom species variance in relation for environmental factors MPI, silt, clay and organic carbon.

4.14 HISTORIC AND MODERN DIATOM COMPARASON

Comparison of historic sample sites (186cm and 193cm), the top of the core (0cm) and a modern site (BSZ4) was undertaken to determine whether differences existed between the three (Table 4.9). Samples from 186cm and 193cm depth of the core were selected for comparison on the basis that they grouped with samples 0cm (surface) in cluster analysis, indicating that they were similar. Samples 186cm and 193cm indicated that they were statistically dissimilar to BSZ4, yet were statistically similar to 0cm (top of the core). Additionally the sample for the top of the core (0cm) was statistically similar to BSZ4. Further analysis of data from each dataset revealed that the abundance of diatom valves found in core samples was noticeable lower than that of the BSZ4 sample site and that BSZ4 contained a higher abundance of fresh water preferring diatom species. Also sample 193cm was much less diverse in species than BSZ4. Samples from the core contained much higher volume of damaged diatom valves than samples taken from the modern estuary indicating that perhaps diatom preservation had been effected during or post burial.

Table 4.9: t-test analysis results comparing historic (186cm and 193cm) diatom samples to modern (BSZ4) and core surface (0cm) diatom sample. Values >0.05 indicates similarity in samples, <0.05 indicates that samples are different.

	Surface Modern	Surface Core	Historic	
	BSZ4	0cm	185cm	193cm
BSZ4	1			
0cm	1.998341	1		
185cm	0.036394	0.235873	1	
193cm	0.027201	0.124382	0.680533	1

4.15 SUMMARY OF CORE RESULTS

One core was collected along the Bridge St transect in the AHE which was then subsampled at intervals of 10cm. Sediment becomes more fined grained from the base to the surface, with one abrupt increase in sand (and larger) sized sediment at 140cm and 160cm. This sand unit is thought to be related to the 1868 Christchurch flood. Caesium dating was undertaken at six points along the core, indicating that caesium related to 1950's nuclear activity appeared between 56cm to 66cm depth. All trace metals show substantial enrichment above 130cm depth as does organic carbon concentration, inferred to be a direct result of industrial activity which began in the 1860's.

All environmental variables were significantly correlated to each other, with the exception of cobalt. Of the forty five diatom species identified ten diatom species assemblages and nine sample assemblages were established using Bray-Curtis dissimilarity cluster analysis (Figure 4.8). By comparing the distribution of sample assemblages and the profiles for each environmental factor (trace metals as pollution indexes, organic carbon and grain size) through the AHE core three separate zones were established (modern, industrial and historic). A distinct change in the composition of the diatom community occurs in response to the onset of industrial activity, while following environmental remediation efforts the diatom community returns to a similar state to that pre-industrial activity.

Spearman's correspondence analyses indicated multiple correlations between key diatom species and selected MPI, organic carbon, sand, silt and clay with p-value ranging of 0.05 to 0.001. All key species correlated with PLI and carbon (Table 4.4). Significant changes were recorded for all environmental factors and in the abundance of *Achnanthes clevei, Cocconeis placentula, Cocconeis scutellum var parva* and *Nitzschia amphibia* between the modern, industrial and historic periods.

CCA results indicate that MPI, organic carbon, silt and clay have less control over diatom species variance (Table 4.7) on a temporal scale compared to a spatial scale. Only 8% (MPI) of the total variance accounted for in all diatom species identified in the AHE core. CCA applied to only the key diatom species (Table 4.8, figure 4.10) recorded no correlation between the variance and the selected MPI, organic carbon, silt and clay, indicating that while they are correlated (Spearman's) some other or multiple other environmental factors i.e temperature, salinity, turbidity are responsible for their change in abundance through the core.

Comparison of a historic diatom assemblage and a modern assemblage found in surface samples taken from the same location as the core was collected (BSZ4) indicate that a significant difference between the two exist. However comparison of historic assemblages and those found in the upper sections of the AHE core were both similar and that the modern assemblage was statistically similar to the same "upper sections" sediment. This discrepancies in correlations indicates that some detrimental influence is limiting how many diatom valves are being preserved post deposition. This is important as it indicates that not all diatom valves are being preserved post deposition, suggesting that core species may not fully reflect the true assemblage at the time of deposition. Therefore some external appears to limit diatom preservation during deposition and possible even pre-deposition. All raw data relevant to chapter 4 is provided in appendices E, F and G.

CHAPTER 6 – DISCUSSION

6.1 EFFECTS ON MODERN DIATOM SPECIES WITHING THE AVON-HEATHCOTE ESTUARY/IHUTAI

Diatom communities were assessed to establish whether any significant variation exists in diatom flora across the AHE and to identify which environmental influences control diatom species distribution. Cluster analysis identified 10 separate diatom assemblages present within the modern AHE. Significant correlations exist between organic carbon and pollution indexes as well as between sediment composition, PLI and MPI. Sediment composition also correlates with organic carbon as well as *Nitzschia amphibia* (sand and silt – $p<0.05$, clay – $p<0.01$). No correlations between sample site elevation and any other environmental factor exist but elevation does correlated with *Cocconeis scutellum var parva* ($p<0.01$). This indicates these specific taxa are responding to elevation and sediment grain size respectively. The distribution of all other key taxa could not be statistically linked to contaminants, grain size, organic carbon or elevation

Kruskal-Wallis analysis was used to determine whether change in the abundance of diatom species or the concentrations of environmental factors varied across the AHE. Only *Navicula perminuta* from the key species and clay statistically differed between transect sites across the AHE. In contrast to this when assessing variance of all diatom species in the modern AHE CCA results indicate that statistically 31% of all diatom species variance can be accounted for within the modern AHE (10% MPI, 11% silt and 10% clay). The remaining 69% of variance recorded in modern diatom species around the AHE is unable to be explained by contaminants, grain size, organic carbon or elevation, raising the question what is causing the observed diatom variation?

All modern diatom data indicates that firstly, modern diatom assemblages do not vary much spatially and the variations do occur are controlled by factors external to the targeted environmental factors of this thesis. Secondly, trace metals, which were hypothesised to cause the majority of variance, only have a minor effect on the distribution and abundance in the modern AHE. Considering that concentrations for trace metals analysed in the modern AHE never rose above what is considered to be harmful levels (ANZESS ISQG-Low guide lines), with the exception of Pb, these results are not surprising. If concentrations were significantly higher this study predicts trace metals may play a much more dominant role in diatom variance.

Visual evaluation of cluster analysis shows site assemblages are grouped by geographical location. Specifically, site assemblages are dependent on whether each site is closer to, (and thus more influenced by) the Avon and Heathcote rivers. Cluster analysis clearly arranges site assemblages into groupings of those near the Avon River (all BS sites) and those closer to the Heathcote River (all Settlers Cres and McCormacks Bay sites), indicated by blue or red boxes in figure 3.10. Southshore sampled species differ from both these two sections, arguably being in a zone more influenced by the marine environment. Variations in river chemistry, flow velocity and salinity due to differing amounts of fresh water being introduced could all be causes for diatom change. In reality due to the complexity of diatom environmental preferences and due to the dynamic nature of the AHE it is likely not going to be any single environmental factor that is responsible for diatom variance. Further study, encompassing a wider range of environmental parameters is needed to get a handle on this situation.

6.2 EFFECTS OF HUMAN SETTLEMENT OF THE AVON-HEATHCOTE ESTUARY/IHUTAI ON DIATOM SPECIES

Research on temporal diatom diversity and abundance change are of great importance as it allows assessment of how human settlement can directly impact the environment of coastal water bodies. One 270cm core was taken from the AHE to allow analysis of changes in diatom abundance and diversity over time. The coring site was located near the modern sample site BSZ4 as this area was away from 2010-2011 earthquake liquefaction sediments and allowed for comparison to a modern sample site.

The AHE core was analysed for pollutants know to be associated with anthropogenic and industrial activity. Pollutants include the trace metals As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn as well as organic carbon and sediment changes. Profiles for each environmental factor (trace metals as pollution indexes, organic carbon and grain size) indicate that each one underwent noticeable amounts of change. Concentrations of trace metals and organic increased substantially between 120cm and 140cm depth. Caesium 137 dating of sediment samples at various depths (28cm, 46cm, 56cm, 66cm, 91.5cm and 140cm) from the AHE core established that the first appearance of ^{137}Cs was between 56cm and 66cm. Caesium 137 spikes are associated with the testing of nuclear weapons that occurred during the 1950's, indicating that sediment between 56cm and 66cm depth was deposited during that time period. Using the ^{137}Cs sediment (56cm-66cm depth) the core depths of other historic events such as the activation of the Bromley treatment facility and the onset industrial activity can be inferred more accurately. Changes in the profiles of environmental factors also helped in placing

historic events. For instance the rapid increase in both pollution index and organic carbon at 120-140cm depth can be linked to the start of the industrial period (~1860's) which corresponds with an absence of Caesium. Similarly Spikes in sand sized sediment between 120cm and 160cm are inferred to be linked to the 1868 Waimakariri flood, while lowering of pollution and organic carbon at 100cm is inferred to environmental remediation efforts in the 1920's (Chapter 4, Table 4.7) with the inception of Bromley works. While these are inferred, rather than absolute age profiles the correlations between ^{137}Cs, and trace elements allow confidence in these interpretations.

Correlations between pollution indexes, organic carbon and sediment grain sizes all record p-values of 0.001. Clay may act as a sink for pollutants (Carman et al 2007) and the same relationship is true for organic carbon and clay (Mayer, 1994). In the AHE core if clay and metals are linked then when clay fractions increase so to would trace metal concentrations. However while clay abundance gradually increases in the AHE core from the base to the top trace metal concentrations exhibit an extremely sudden increase in concentration between 140 and 120cm depth, recording enrichments between 17.5% (Mn) up to 634% (Cd). It stands to reason that if clay was the primary controlling factor on trace metal concentration in the AHE trace metals would exhibit a more gradual enrichment mirroring that of clay. This however is not the case so the trace metal spikes must be caused some other factor. Further evidence that these are likely not related is seen at the top of the AHE core. Trace metal concentrations start decreasing rapidly between 30cm and 40cm while clay continues to become more abundant. A much more likely cause for trace metal and organic carbon increase in the AHE core is anthropogenic activity. Industrial activity would allow for a rapid increase in both factors concentration, furthermore many of the trace metals included in this study are known to be produced by industrial activities which took place between the 1860s and the 1980s.

Correlations also occur between key diatom species and environmental factors (sediment, pollution and organic carbon) within the AHE core. Five key species (*Achnanthes clevei, Cocconeis placentula, Cocconeis scutellum var parva, Navicula perminuta* and *Nitzschia amphibia*) were selected due to each being present throughout most of the AHE core and in modern sample sites. All five species record correlations ($p<0.05$ to 0.001) with at least one environmental factor and usually multiple. Correlations between key diatom species and environmental factors indicate that direct relationships exist between diatoms in the AHE and anthropogenic activities. No other studies exist which study New Zealand estuarine diatom communities and their response to anthropogenic to make comparisons with. This study therefore extends the understanding of anthropogenic effects on diatom communities in New Zealand estuarine environments.

The AHE core was partitioned into three sections pertaining to human activities which have had major impacts on the environment: a) Modern – after all major pollutants ceased to be discharged into the AHE, b) industrial – encompassing the industrial period, c) historic – pre industrial activity). Statistical analysis using Kruskal-Wallis analysis on the concentrations of environmental factors and the abundance of diatom species in each zone show that each has changed. An interesting pattern is noticeable when sample site assemblages produced using cluster analysis are superimposed over pollution profiles (Chapter 4, Figure 4.9). In the historic zone four site assemblages occur together, these being site assemblages A, D, H and I. In the industrial zone only site assemblages B, C and E are present and in the modern zone site assemblage D reappears while site assemblages G and F make their first appearance. Figure 4.9 shows that at the onset of industrial activity (140cm – 120cm, roughly 1860s) where pollution concentrations increase rapidly a distinct response in seen in the diatom community, expressed as a complete change in diatom site assemblages. Site assemblage D, which is considered representative of a natural non-anthropogenically altered diatom habitat then reappears after environmental remediation processes have been undertaken. Environmental remediation processes include the activation of the Bromley treatment facility (1965) and the stopping of industrial effluent from been discharged directly into the AHE (1981). Therefore not only do the changes in site assemblages show that industrial activity had a direct impact on AHE diatom communities over time, but also that remediation efforts have successfully returned the AHE environment to a similar state as it was pre-European settlement.

Further statistical analysis on the abundance and distribution of diatoms though the core indicated that the selected environmental factors (MPI, silt, clay and organic carbon) account for even less diatom variance than they do in the modern AHE. Of the total variance recorded by all diatom species present only 8% is accounted for (MPI, $p<0.05$). When key species are analysed none of the variance recorded is accounted for by environmental factors. Therefore if trace metals, organic carbon and sediment variations are not responsible for diatom variation through the AHE core this raises the questions A) why not? And B) what is responsible? Originally this study's hypothesis was that trace metal variation would be the dominant driver of diatom community variation. However, although trace metal concentrations are shown to be enriched by industrial activity they still (mostly) remain below ANZECC ISQG-Low guidelines. The only trace metal that rises above soil contamination guidelines is Pb, which stays above the ISQG-Low threshold throughout the industrial period. Literature pertaining to the effect of trace metals on estuarine diatom communities are exceedingly rare; more studies have been undertaken on trace metal effects on diatoms inhabiting lakes and rivers yet even these still have a limited abundance. The presence of trace metals in sediments inhabited by benthic diatom have been linked to alterations in both diatom abundance and diversity in lakes and

rivers (Cattaneo et al. 2008; Ferreira da Silva et al. 2009; Medley and Clements 2011). Each study indicated that diatom communities were affected by the presence of trace metals. However concentrations recorded in studies where change was observed were at minimum one order of magnitude larger and usually multiple orders higher than concentrations recorded in both the modern AHE and through the core. This likely explains the relative lack of correlations between changes in trace metals and diatom species described earlier.

Estuaries are inherently complex and extremely dynamic areas which make controlled experiments much more difficult to undertake than comparative studies in other more stable locations such as lakes. Due to this difference applied diatom studies in coastal water bodies such as estuaries are rare, especially compared to diatom paleolimnology. Never the less some studies have been undertaken and my provide insight into what "unknown" environmental factors influence diatom variance within the AHE. Changes in water temperature have been found to effect the turnover of benthic diatom communities (Hillebrand et al. 2010; Underwood et al. 1998). While larger diatom species such as *Achnanthes brevipes* have also been observed to increase in abundance when water temperatures increase. Within the AHE *A.brevipes* valves in sediment samples are absent in the lower half of the core and are only found in the upper half and in modern AHE sediment samples. Silica concentrations in solution, if low, can inhibit diatom community growth. Furthermore silica depletion can induce major changes in diatom species compositions. Soluble silica can be supplied to estuaries through sewage effluent as well as deforestation (Conley et al. 2008). Both deforestation (historically) and effluent discharge (recently) have occurred in and around the AHE. Thus changes in silica concentrations in the AHE could play a part in diatom abundance through the core. Changes in diatom abundance through the AHE core may indicate that silica in the AHE has increased during and after the industrial period. Nutrient load in estuaries has also been linked to changes in diatom community's spatial and temporal distribution (Smol and Stoermer 2010), and this may also be important to AHE diatom species.

6.3 HISTORICAL DIATOM ASSEMBLAGES

To determine whether diatom communities within the modern AHE and the historic zone of the AHE are similar, core sediment samples from depths of 186cm and 193cm were compared with the modern BSZ4 sample site. Core samples at 186cm and 193cm were selected on the grounds that they grouped together with samples from the top of the core (0cm and 16cm) in cluster analysis. Statistical approaches towards determining similarity between historic (186cm and 193cm) and modern diatom compositions from BSZ4 that no similarity exists ($p<0.05$). Historic samples were statistically similar to samples at the top of the core (0cm). Diatom abundance in samples 0cm, 186cm

and 193cm were much lower than that of BSZ4. The presence of additional fresh water/ low salinity preferring diatom species such as *Hantzschia amphioxys* and *Achnanthes brevipes* combined with the higher abundance of fresh/low salinity preferring species (*Achnanthes clevei*, *Cocconeis placentula*, *Navicula cryptotenella* and *Nitzschia amphibia*) in BSZ4 indicates that salinity may have been higher as the historic zone was being deposited.

Possible processes which may cause differences in species between the modern BSZ4 and the historic assemblage zone could be A: During deposition the historic zone was closer to the marine interface or further away from any fresh water input (or both) than its modern counterpart. The period of time which divides the historic assemblage and its modern counterpart is roughly 200 years. Yet in the recorded history neither the Avon river mouth nor the AHE itself altered their location substantially. Thus the site where the historic zone was deposited is assumed to be fairly similar to that of its modern counterpart. Urbanization may provide an explanation for decreasing salinity through the AHE core. Buildings, roads and pavement increase surface runoff of fresh water supplied via rain fall, which instead of being absorbed into soil discharges directly into the nearest water body (the AHE). Therefor over time the amount of fresh water being discharged into the Avon River and the AHE may have increased as urbanization occurred. Additionally for a long period of time the Bromley treatment facility discharged its treated waste directly into the AHE, providing a huge amount of fresh water. This means that post European arrival the amount of fresh water mixing with saline water has been increasing, allowing salinity levels to drop over time.

By comparing the abundance of diatom valves in samples BSZ4, 186cm and 193cm it was found that samples from the historic zone had a much lower abundance than BSZ4. Diversity of diatom in the same samples indicated that 193cm (H=1.974) was much less diverse than BSZ4 (H=2.355) but 186cm (H=2.478) had about the same level of diversity, although species present differed substantially. Within the samples 186cm and 193cm many fragmented valve pieces were observed, most of which were too small for species or genus identification. As has been stated earlier, statistically samples 186cm and 196cm differ from BSZ4, yet are similar to 0cm. Additionally BSZ4 and 0cm are statistically similar. These observations suggest a trend where preserved diatom species gradually change as deposition occurs. Degradation of diatom valves and the gradual loss of similarity between samples from the surface to the historic zone implies that one or more processes have occurred during or post deposition which effects diatom valve preservation.

Mechanical and chemical destruction of diatom valves occurs when particular environmental conditions are present (Smol and Stoermer 2010). Mechanical destruction occurs when diatom valves are subjected to intertidal exposure or abrasion in high energy environments (Hemphill-haley 1995).

Additionally re-suspension and transportation as well as predation of diatoms can lead to the fragmentation of diatom valves (Cooper 1995; McClatchie et al. 1982; Stoermer and Smol 2001).

Chemical dissolution of diatom valves is another factor to consider, a process which is found to be prevalent in highly alkaline or saline waters (Barker et al. 1994; Smol and Stoermer 2010). As a result of urbanisation of the land surrounding the AHE, increased amounts of fresh water has likely been discharged into the AHE and associated tributaries. A further source of fresh water came from treated effluent discharged out of the Bromley treatment facility directly into the AHE. With elevated levels of fresh water being supplied to the AHE, salinity levels would have dropped thereby reducing the likelihood of silica dissolution in the AHE. Alternatively an increase in the preservation potential of silica occurs as pH decreases or organic carbon increases in sediments. Over the period of European settlement organic carbon concentrations have increased in AHE sediments. Increased nutrient levels and decreased pH levels have been shown to assist in preservation of siliceous materials in estuarine sediments (Reid et al. 2008). Another consideration for differences in modern and core diatom species is that freshwater species will usually be more silicified than marine species allowing freshwater species to be better preserved (Conley et al. 1989).

CHAPTER 7 - CONCLUSION

Diatom communities in the modern Avon-Heathcote Estuary/Ihutai are diverse and high in species abundance. Across the Estuary, diversity of diatom communities is relatively stable, indicating that relatively little variance is occurring between transect sites, and even less between sample sites within transects. Overall 31% of the variance recorded within the diatom community can be accounted for by MPI, silt and sand. The environmental factors which this study elected to focus on (trace metal concentration, organic carbon concentration, sediment composition and elevation) have little to no control. It is apparent that while diatom communities of the modern AHE are stable and relatively similar across its area. The little variance that is observed is caused by an environmental factor not analysed in this study. Grouping of site assemblages indicate that proximity to the source waters of the Avon or the Heathcote rivers may be a strong factor influencing in how diatom communities are arranged in the AHE. Further study on a much wider scale including more environmental parameters such as detailed temperature and salinity reading, yearly diatom cycles, nutrient load and turbidity, with a more detailed focus is needed to further understanding in area.

While diatom species through the AHE core correlate significantly with MPI, silt, clay and organic carbon, only 8% of the diatom variance from pre-European influence sediments to the modern day can be accounted for by these factors. Over this same period, geographically, AHE has changed minimally; however human land use and anthropogenic activities have changed significantly during this time. Environmental factors such as changes in silica, nutrient load, temperature and salinity likely contribute to some of the unaccounted variance recorded. Cluster analysis indicates that the industrial period has had a noticeable impact on diatom communities in the AHE. A complete change in the diatom community is recorded during the industrial period, whereas environmental remediation over the last 100 years has been successful in returning the AHE to a similar ecological state to pre-European settlement. This is reflected by the diatom community at the top of the core, which is similar to that which is found in sediments that were deposited before European settlement.

Finally preservation of diatom valves have improved over time. Samples in the modern Estuary and those from sections of the core which were deposited after the onset of the industrial period have a higher diversity of diatom species and abundance of preserved valves present. This has occurred as organic carbon levels within the AHE have increased due to industrial activity, assisting in the preservation of diatom valves.

Future work must be undertaken in order to understand exactly what factors are responsible for diatom change over both a spatial and a temporal scale. These studies should include a wider range

of environmental factors known to be influenced by anthropogenic activity, as well as multiple core studies and a broader range of modern sample sites.

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CHAPTER 9 - APPENDICIES

All Appendices are provided electronically.

Appendix (A) – Modern diatom data

Appendix (B) – Modern trace metal, elevation and sediment data

Appendix (C) – Modern organic data

Appendix (D) – Modern environmental data

Appendix (E) – Core diatom data

Appendix (F) – Core trace metal data

Appendix (G) – Core organic and sediment data